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THE OCCURRENCE OF FLUORIDES IN ALBERTA WATERS  
AND A STUDY OF METHODS FOR REMOVING THEM.

by

Gordon R. Finlay, B. Sc.

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THESIS

THE OCCURRENCE OF FLUORIDES IN ALBERTA WATERS  
AND A STUDY OF METHODS FOR REMOVING THEM.

Submitted in partial fulfilment of the requirements  
for the Degree of Master of Science.

by

Gordon R. Finlay, B. Sc.

under the direction of Dr. O. J. Walker

Time devoted to thesis work was 5.3 out of 7.0 months  
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## INTRODUCTION

Mottled enamel of the teeth was first observed and recorded by Capt. Eager (7) in 1901 as appearing in the teeth of emigrants leaving Italy for the U. S. A. This tooth defect was not again considered until it was described by Black and McKay in 1916. During subsequent years these workers proved that the occurrence of this disease was related in some way to the drinking water supply.

Manganese was suspected as the causative agent, but in 1931, Smith, Lantz and Smith (10a and b) produced very definite evidence of a correlation between fluorides in the water supply and the incidence of mottled teeth in the district of St. David, Arizona. Churchill (23) at about the same time presented similar data covering a wide area in the U.S.A. Previously McCollum and co-workers had observed the effect of fluorides on the teeth of rats, but no correlation of this with mottled enamel was made (5).

"Chronic dental fluorosis" is thus the equivalent of "mottled enamel" and is the first indication in the human being of chronic fluoride intoxication. The mottling of the teeth varies with the fluoride content of the water supply--chalky-white spots appear when the water contains 1 or more p.p.m. fluoride (p.p.m. = parts per million parts of water)--the color deepens through yellow to brown and black as fluoride content rises to 4 or 5 p.p.m. and at higher values, corroding, pitting



and complete loss of enamel occur.

Dean has concluded (4) from exhaustive observations on affected teeth and water-supply histories for each case, that the mottling is produced during the period of calcification before the teeth erupt. Deciduous teeth are rarely affected. This, of course, follows from the fact that the calcification of such teeth is well advanced at birth--in some cases may be well-nigh complete. In any event, mottling of deciduous teeth is not of serious import.

The permanent teeth are calcified between the ages of 0 and 12 years with the exception of the third molars (4) and this, then, is the period during which control of the fluoride content of the drinking water is important. The susceptibility of various individuals seems to vary with their calcium metabolism. The actual intake of fluorides may vary from person to person and from family to family depending on one's cooking or drinking habits. However, the threshold value of 1.0 p.p.m. of fluorine in the drinking water seems to be well established (41)(15c) as that at which the first signs of dental fluorosis appear.

Gautier and Clausmann (6) expected that it would be found that fluorine played a role in animal metabolism. No very good evidence for this has been adduced. However, it has been shown (5) that fluorides have an effect on the action of certain enzymes--e.g. phosphatase and lipase.



Dean has recently (14d) compiled statistical evidence to show that the incidence of caries is lower than average in persons who have mottled teeth. This had previously been hinted at by a number of investigators. Further investigation of this relation is necessary before any conclusions may be drawn, but it seems possible that a certain quantity of fluorine may be required for sound enamel structure. On the other hand (4) a large excess of fluorine definitely causes complete loss of enamel.

Fluoride intoxication occurring in adults has no effect upon the teeth, but the fluorine content of the bones is increased. Roholm (19) has observed bone affections (osteosclerosis) among cryolite workers. An area in southern India has been reported (20) in which a high fluorine content of the drinking water is said to be the cause of bone and joint maladies in adults. It has been observed at Granum, Alberta, that an unusually large number of broken bones occurred among the children. This has also been attributed to the effect of fluorides.

A number of animals exhibit fluorine intoxication. The effect on the bones and teeth of swine and rats has been observed by Bethke et al. (13) and others. A great deal of the experimental work on "dental fluorosis" has been done on the rat (10)(5). Mottled enamel has been observed in cattle (14b), dogs and horses.

The effect on plants has been studied but the evidence is quite conflicting (12, 6, 18). Fluorides have an effect on the utilization of phosphates by the



plant. This fact is important in the fertilizer industry. Aside from this the effect of fluorine seems to be injurious to some plants, beneficial to others.

Surveys have shown that dental fluorosis is endemic in parts of all continents but Australia, on which no reports are available. India, Great Britain, Russia, Germany and France are among those countries in which endemic areas have recently been found. In Canada, Alberta (11) is the only area which has been surveyed. Persons who spent their childhood in Saskatchewan, Manitoba or Eastern Canada have been examined and have been found to be afflicted with mottled enamel. This would lead one to believe that there are endemic areas in other provinces. It seems strange that in the United States, Montana, bordering on Alberta, is one of the few states in which no endemic areas have yet been reported. The most severe cases on this continent have been observed in Arizona (4).



The research to be reported in this thesis continues the survey of "mottled enamel" and fluorine content of the water supply which was initiated by Walker and Spencer in 1935 (11) and the work on removal of fluorides from drinking water begun by Walker and Harris in 1937 (58).

The survey has been continued in an endeavor to mark out the areas in which a detailed survey should be conducted.

Attempts have been made to correlate the source of supply and the type of water with the fluoride content.

Simple and efficient methods of removing fluorides from water have been sought such as would be applicable to treatment of individual domestic water supplies.

It was found necessary to modify the analytical methods in order to deal with certain water-supplies of unusual nature. Special procedures were also required in some experiments on the removal of fluorides.

A number of soils have been examined for fluorine content and a method of analysis has been described which is believed to be suitable.



## ANALYTICAL

### Water Analysis

Fluorine has been frequently reported as a constituent of natural waters. It was found in the springs at Vichy as early as 1873. Hillebrand determined fluorine in water from Ojo Caliente, New Mexico, in 1893 (1). Gautier and Clausmann, precipitating fluorine as lead chloro-fluoride, determined fluorine in many mineral waters in France in 1914. This was the first accurate method used for determining small amounts, but the procedure is long, expensive and intricate.

Since precipitation methods appeared to be unsatisfactory, the formation of complexes was investigated. Steiger (43) developed a colorimetric method based on the fading of the orange color of titanium peroxide in the presence of fluorides. This action is believed to be due to the formation of a complex. Foster (28) devised a similar method involving the fading of the color of ferric thiocyanate due to the formation of the  $\text{FeF}_6^-$  complex. Sanchis (39) developed a method suitable for water analysis from earlier methods of De Boer, Casares, and Thompson and Taylor. This colorimetric method depends upon the fading of the zirconium lake of the dye, sodium alizarin sulfonate, in acid solution, by the formation of the complexes  $\text{ZrF}_5^-$ ,  $\text{ZrF}_6^-$ ,  $\text{ZrF}_7^-$ , etc. A similar method, due to Kolthoff and Stainsby (31) employing purpurin as the dye, in place of the alizarin derivative, has received little attention. Gad and Naumann (29) have recently



given alternative procedures for the Sanchis method and have also used hematein (derived from hematoxylin) for forming a zirconium lake, which behaves in a manner very similar to the Sanchis indicator. A translation of the three new procedures these workers have devised is given below since it is not elsewhere available.

"Method 1

To 100 c.c. water, add 12.0 c.c. of an acid zirconium nitrate solution (prepared by mixing 50 c.c. N sulfuric acid, 50 c.c. N hydrochloric acid and 1.7 c.c. of 0.87% crystallized zirconium nitrate solution.) Add to this 1.0 c.c. of a 0.033% solution of sodium alizarin sulfonate. Comparison solutions are prepared similarly. After standing 4 hours or over-night at room temperature, read colorimetrically.

"Method 2

Reagents.

To 78 c.c. distilled water, add 2.0 c.c. of a solution of 0.87 gm. crystallized zirconium nitrate in 100 c.c. distilled water and 20 c.c. of a 0.1% hematoxylin solution which has stood for several days and is orange in color. After standing 24 hours, the dark violet solution is ready for use. This reagent may be kept in a brown bottle.



Directions for use.

To 50 c.c. water add 2.0 c.c. of the above reagent and 6.0 c.c. of a mixture of equal parts N sulfuric acid and N hydrochloric acid. Prepare similarly comparison solutions over the range 0.0 - 3.0 p.p.m. of fluoride. After standing 2 hours or else over-night, read colorimetrically.

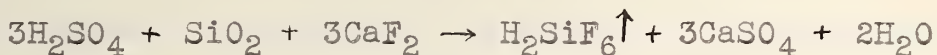
"Method 3

To 50 c.c. water, add 6.0 c.c. of the acid zirconium nitrate solution (see above), and 1.0 c.c. of a solution of 0.020 gm. hematoxylin in 100 c.c. water, which has stood for several days. Prepare in the same manner standards of known fluoride content ranging from 0 to 3 p.p.m. Allow to stand 4 hours or else over-night and compare colorimetrically."

Willard and Winter (44) devised a titration method in which the Sanchis indicator was employed in titrating a solution containing fluoride. The titration was made with thorium nitrate, a precipitate of thorium fluoride being formed. The end point was indicated by the appearance of the red color of the zirconium lake. It was found later that the zirconium was unnecessary as the thorium lake could be formed. This method was adapted to water analysis by Boruff and Abbot, by Armstrong (21) and by Walker and Spencer (11). The titration is preceded by a distillation in the presence of



silica to separate interfering elements, fluorine distilling over from an acid solution as hydrofluosilicic acid.



Numerous modifications have recently been made in this procedure to adapt it to various purposes (30, 33, 35, 36, 37, 38).

Churchill (23) and others (22) have determined fluorine spectroscopically by means of the distinctive calcium fluoride band.

In this laboratory a modified Sanchis method and a modified Armstrong method have been employed for some time (11) on a wide variety of water samples.

At present the modified Sanchis method is used as follows. A sample of 100 c.c. of water is taken and to this are added 2.0 c.c. of 3.0 N hydrochloric acid, 2.0 c.c. of 3.0 N sulfuric acid, and 1.80 c.c. of indicator solution (made up to contain 0.17 mg. of sodium alizarin-sulfonate and 0.87 mg. of C.P. zirconium oxy-nitrate,  $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  per c.c.). The solution is heated just to boiling, allowed to stand over-night and compared with standards containing 0.0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 and 1.5 p.p.m. fluorides which are treated in the same manner. The range may be extended by taking an aliquot of the original sample, diluting to 100 c.c. and multiplying by the factor required. Great care must be taken in measuring the sulfuric acid, as sulfates affect the color of the lake. The amount of indicator is also important.



Results obtained by this method failed to agree in a number of cases with those obtained by the modified Armstrong method as described in (11). Difficulties were also met in applying one method or the other to fluoride-removal experiments which were in progress. It was believed that either or both of the methods were affected by dissolved substances in the water so it was deemed advisable to tabulate the variations in dissolved salt content which might be expected in the waters of Alberta.

The table below lists the constituents which have been found in Alberta waters used for drinking purposes and the range of concentrations observed.

Table I

Composition of Typical Alberta Waters

|                          |                                            |
|--------------------------|--------------------------------------------|
| Total Solids             | 200 - 10,000 parts per million             |
| Loss on ignition         | 0 - 600                                    |
| Total Hardness           | 0 - 1000 (Calcium and Magnesium)           |
| $\text{SO}_4^{=}$        | 0 - 8000                                   |
| $\text{Cl}^-$            | 0 - 200                                    |
| Alkalinity               | 0 - 1200                                   |
| $\text{Na}_2\text{CO}_3$ | 0 - 1500                                   |
| Al and Fe oxides         | 0 - 50                                     |
| $\text{Fe}^{++}$         | 0 - 2 (to 100 in rarely-found acid waters) |
| $\text{Fe}^{+++}$        | 0 - 2                                      |
| Colloidal Fe             | 0 - 40                                     |
| $\text{Mn}^{++}$         | 0 - 2                                      |
| $\text{P}_2\text{O}_5$   | 0 - 20                                     |
| $\text{SiO}_2$           | 0 - 35                                     |
| $\text{F}^-$             | 0 - 5                                      |



There may also be present borates, iodides, lithium, potassium, and, of course, small amounts of ammonia, nitrates and nitrites.

In the light of this information it was decided to carry out a series of determinations to identify the interfering substances and to devise methods of analysis which would give satisfactory values for the fluorine content. The results of the determinations are presented in Table II and Figure I.

It is plain from these results that aluminum, iron, phosphates and sulfates may cause serious errors in the determination of fluorine by the Sanchis method. The effect of sulfates is additive, so that a correction may be applied if the amount of sulfates present is known. In general, 300 p.p.m.  $\text{SO}_4^{=}$  is equivalent to 0.1 p.p.m.  $\text{F}^-$ , although for very large amounts of sulfates the effect is not as great proportionally. Corrections may be made by the use of Figure I. Application of this correction for sulfates brings the Sanchis results into agreement with those obtained by the modified Armstrong method in more than half the cases in which a difference between the results for the two methods was found. In the remainder of these cases of discrepancy, the Armstrong method results are higher than those for the Sanchis method. Such a situation may be due to the presence of aluminum or phosphates or iron in the samples. The effect of aluminum on the Sanchis method (see Table I) is to give low results if more than 4 p.p.m. be present. Iron above 5 p.p.m.



Table II

Effect of Added Substances on Modified Sanchis Method

Mn<sup>++</sup>      A saturated solution of MnO<sub>2</sub>.H<sub>2</sub>O destroyed the indicator.

| F added<br>in p.p.m. | F found                   |               |
|----------------------|---------------------------|---------------|
|                      | +1 p.p.m. Mn <sup>+</sup> | +2 p.p.m. Mn. |
| 0.5                  | 0.5                       | 0.5           |
| 1.0                  | 1.1                       | 1.0           |

Effect of amounts found in natural waters is negligible.

Norite      No effect in alkaline solution. Removes F<sup>-</sup> in acid solution below pH 3.0 (54). Norite is useful in decolorizing certain samples if used in alkaline solution.

|          |     | <u>Al<sup>+++</sup> added in p.p.m.</u> |     |     |     |     |     |     |     |
|----------|-----|-----------------------------------------|-----|-----|-----|-----|-----|-----|-----|
|          |     | 0.2                                     | 0.4 | 0.6 | 1.0 | 2   | 5   | 10  | 18  |
| Fluoride | 0.5 | 0.5                                     | 0.5 | 0.5 | 0.5 |     |     |     |     |
| Added    | 1.0 |                                         |     |     |     | 1.0 | 0.7 | 0.6 | 0.5 |

Al ion causes low results if present over 4 p.p.m.

|             |  | <u>Fe<sup>++</sup> added in p.p.m.</u> |     |     |     |     |
|-------------|--|----------------------------------------|-----|-----|-----|-----|
|             |  | 0.5                                    | 1   | 2   | 5   | 10  |
| 0.5 F added |  | 0.5                                    | 0.6 | 0.6 | 0.6 | 0.7 |

|             |  | <u>Fe<sup>+++</sup> added in p.p.m.</u> |     |     |     |           |           |       |       |       |
|-------------|--|-----------------------------------------|-----|-----|-----|-----------|-----------|-------|-------|-------|
|             |  | 0.5                                     | 1   | 2   | 3   | 4         | 5         | 10    | 20    | 40    |
| 1.0 F added |  | 0.9                                     | 0.9 | 0.8 | 0.9 | off color | off color | clear | clear | clear |

SiO<sub>2</sub>      added as soluble Na<sub>2</sub>SiO<sub>3</sub>.

|             |  | <u>SiO<sub>2</sub> added in p.p.m.</u> |     |     |     |     |     |
|-------------|--|----------------------------------------|-----|-----|-----|-----|-----|
|             |  | 4                                      | 8   | 20  | 40  | 80  | 160 |
| 0 F added   |  | 0                                      | 0   | 0   | 0   | 0   | 0   |
| 0.5 F added |  | 0.6                                    | 0.4 | 0.4 | 0.3 | 0.5 |     |



Table II (cont'd.)

Cl<sup>-</sup> added as MgCl<sub>2</sub>.

|                       | <u>F added</u> |     |     |     |
|-----------------------|----------------|-----|-----|-----|
|                       | 0.8            | 1.0 | 1.2 | 1.5 |
| +500 Cl <sup>-</sup>  | 0.7            | 0.9 | 1.1 | 1.5 |
| +1000 Cl <sup>-</sup> |                |     | 1.1 | 1.4 |

Na<sup>+</sup> added as NaOH 200 p.p.m. had no effect on F<sup>-</sup> solutions. Added as NaCl.

|                      | <u>F added</u> |     |     |     |     |     |     |
|----------------------|----------------|-----|-----|-----|-----|-----|-----|
|                      | 0.2            | 0.4 | 0.6 | 0.8 | 1.0 | 1.2 | 1.5 |
| +100 Na <sup>+</sup> | 0.2            | 0.3 | 0.6 | 0.8 | 1.0 | 1.2 |     |
| +200 Na <sup>+</sup> |                | 0.4 | 0.6 |     | 1.0 |     |     |
| +500 Na <sup>+</sup> |                |     | 0.6 | 0.8 |     |     | 1.5 |

Na<sub>2</sub>CO<sub>3</sub>

|                                     | <u>F added in p.p.m.</u> |     |     |     |     |     |     |
|-------------------------------------|--------------------------|-----|-----|-----|-----|-----|-----|
|                                     | 0.2                      | 0.4 | 0.5 | 0.6 | 0.8 | 1.0 | 1.2 |
| Na <sub>2</sub> CO <sub>3</sub> 100 | 0.1                      | 0.4 |     |     | 0.8 |     |     |
| 200                                 | 0.1                      | 0.3 |     | 0.6 | 0.7 | 1.0 |     |
| 500                                 |                          |     | 0.5 | 0.4 |     |     | 1.1 |
| 1000                                |                          |     | 0.5 |     |     |     |     |

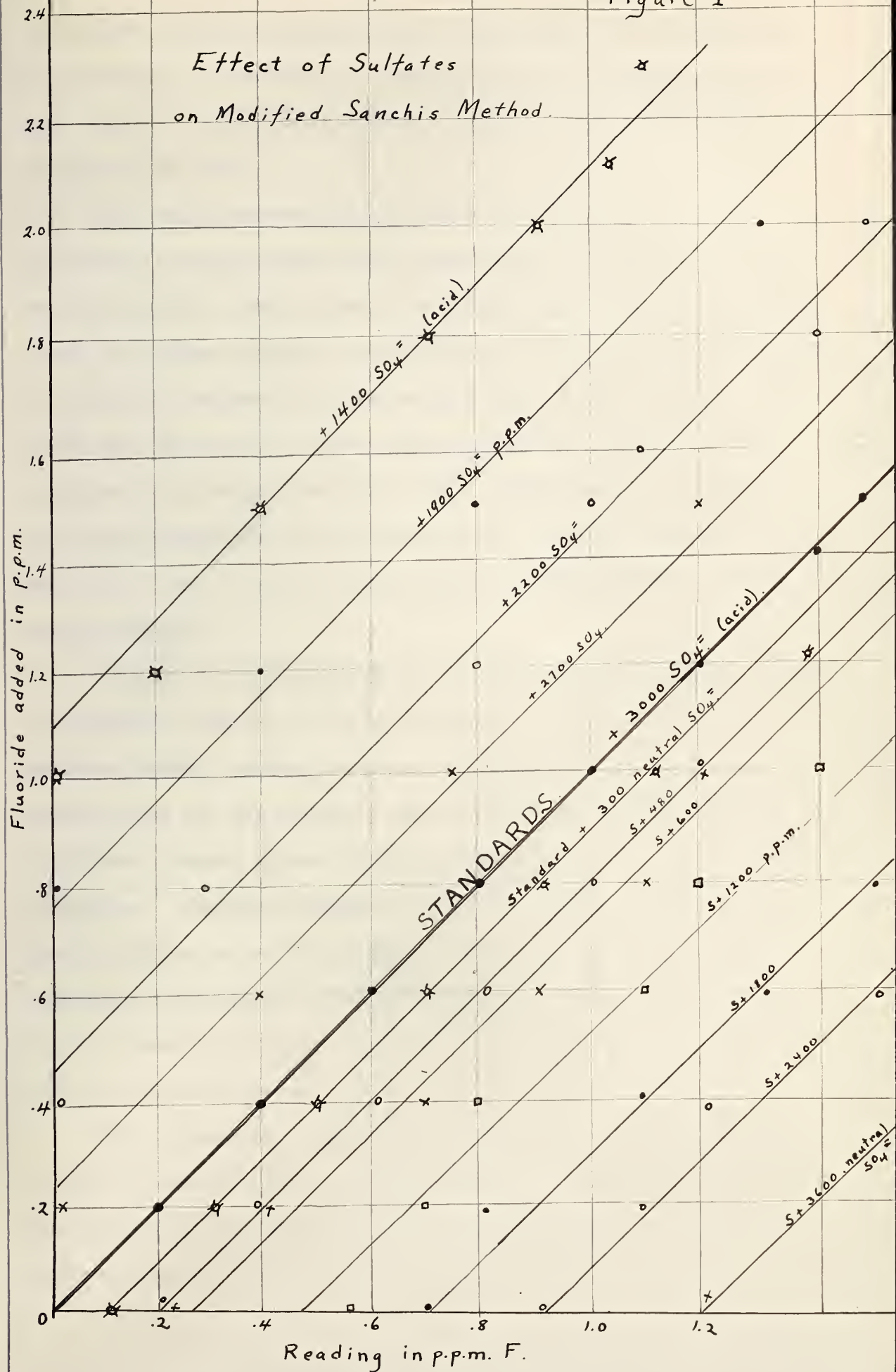
P<sub>2</sub>O<sub>5</sub>

| P <sub>2</sub> O <sub>5</sub> (p.p.m.) | <u>F added in p.p.m.</u> |     |     |      |
|----------------------------------------|--------------------------|-----|-----|------|
|                                        | 0.0                      | 0.5 | 1.0 | 1.5  |
| 2                                      | 0.1                      | 0.4 | 0.8 |      |
|                                        | 0.1                      | 0.5 | 0.8 |      |
|                                        |                          | 0.5 | 0.8 |      |
| 5                                      |                          | 0.6 | 0.6 |      |
|                                        | 0.2                      | 0.4 | 0.5 | 0.9  |
|                                        | 0.2                      | 0.0 | 0.5 | 0.9  |
|                                        | 0.0                      | 0.3 | 0.7 |      |
|                                        |                          | 0.5 | 0.7 |      |
| 10                                     |                          | 0.5 |     |      |
|                                        |                          | 0.4 | 0.8 |      |
|                                        | <0                       | 0.5 | 0.5 | 0.9  |
|                                        | <0                       | 0.1 | 0.7 | 0.9  |
|                                        |                          | 0.2 | 0.7 |      |
| 15                                     |                          | 0.5 |     |      |
|                                        |                          | 0.7 |     |      |
|                                        |                          | 0.8 |     |      |
| 20                                     |                          | 0.5 |     |      |
|                                        | <0                       | 0.8 | 0.8 | 1.5  |
|                                        |                          | 0.5 | 1.2 |      |
|                                        |                          | 0.8 |     |      |
| 30                                     |                          | 1.0 | 1.5 | +1.5 |

Fluoride found.



## Effect of Sulfates on Modified Sanchis Method





destroys the indicator color. The effect of phosphates (see Table) is erratic. Interference by silicates does not seem to be as serious as some investigators would suggest (29, 39).

The data presented in Figure I on the effect of sulfates do not agree with those given by Scott and co-workers (55). The correction values which these workers list are given beyond the accuracy of the method, so that it does not appear by what means they were obtained. Dean and Elvove (3) give corrections for sulfates to be applied to Elvove's method (25). This method, however, is very sensitive to the action of sulfates and is, in any case, only suitable for routine measurements on one water-supply.

It may be observed from the graph showing the action of sulfates, that, if only one c.c. of the 3N sulfuric acid be added to the samples in place of the two c.c. prescribed by the method, then the color change of the indicator takes place over the range 1.0 - 2.5 p.p.m. of fluorine. Samples treated in such a way might be compared either with the regular standards or with a set of standards prepared in the same manner. The color change is the same in either case and is due to the combined effect of sulfate and fluoride.

The procedure suggested above gives more accurate results than the simpler expedient of taking an aliquot and diluting to volume, which is otherwise required to extend the modified Sanchis method above 1.5 p.p.m. fluorine.



An attempt to remove sulfates prior to analysis by precipitation as barium sulfate was unsatisfactory, especially since any excess  $\text{Ba}^{++}$  precipitates the sulfate added as sulfuric acid. It is simpler to determine sulfates and make the correction.

The modified Armstrong method was at first employed as described by Walker and Spencer (11). High results were obtained in cases where phosphates were present; and it was found necessary to employ 25 c.c. of 60% perchloric acid for the distillation in place of the sulfuric acid, if phosphates were present in appreciable quantity. A double distillation with sulfuric acid gave fairly good results.

Some confusion has arisen over the amount of indicator required for titration. Armstrong (21) used three drops of 0.05% solution of sodium alizarin sulfonate. Boruff and Abbott used about six times as much. Spencer apparently used six drops of the 0.05% dye solution in this laboratory but his report states six drops of 0.5% solution. Harris obtained good results with this quantity and it was used for some time but later three drops of 0.5% solution were found to be quite sufficient. Under these conditions the color change is from greenish-yellow to brown.

Hoskins and Ferris (30) have used a buffer to maintain a constant pH during the titration with thorium nitrate. The buffer contains 0.4 moles of monochloroacetic acid and 0.4 moles of sodium chloroacetate in one



litre and is used at the rate of one c.c. to each 20 c.c. of titration solution. It has been in use in this laboratory for the past two months and is of considerable assistance either in alcoholic or water solution.

Armstrong and others (33, 36) have obtained good results by titrating in water solution. Standard solutions treated in this way gave excellent results, but unknown samples gave high results, unless distilled with perchloric acid rather than sulfuric acid.

It is therefore recommended for water samples that distillation be made with sulfuric acid followed by titration in alcohol; or, if phosphates are suspected of being present, distillation be made with perchloric acid and titration follow in water solution.

The zirconium-hematoxylin method (29) has been tested on a few samples. It is subject to the same limitations in general as the Sanchis method, being slightly more affected by iron and aluminum. It does not seem to be as sensitive to fluorine as has been claimed, nor is it as sensitive as the modified Sanchis method. It is, however, simpler than the latter and deserves further study.

Colored waters have been successfully analysed by the Sanchis method after decolorization with norite in neutral or alkaline solution (see Table II and McKee and Johnston (54)). Alternatively they may be distilled as in the Armstrong method and then analysed by either the Sanchis method (29) or the usual titration procedure.



Colloidal clay in waters may be precipitated out by adding the acids as given in the Sanchis procedure and allowing the sample to stand over night. The clay precipitates and may be filtered off. The indicator is then added and the remainder of the procedure carried out.

Summarizing the methods for water-analysis, it may be said that:

(1) The modified Sanchis method is suitable for most potable waters, if a correction for sulfates be applied. Iron, aluminum and phosphates interfere seriously.

(2) The effect of iron and aluminum can be eliminated by using the modified Armstrong method, distilling with sulfuric acid. If a precipitate of hydrated iron oxide tends to form from the natural water it tends to carry down with it part of the fluorine and thus lower the fluoride concentration. In analysing such waters a perfectly fresh sample is required for a true analysis.

(3) The effect of phosphates can be eliminated by distilling with perchloric acid in the modified Armstrong method.



### Soil and Rock Analysis

Steiger's procedure (43) was tried out on a number of soils but no fluorine was found in any in sufficient quantity to give results by this method. The spectroscopic method was attempted but no arc carbons were available which would give a satisfactory blank. Apparently arc carbons contain considerable amounts of zirconium fluoride. Snell (42) gives a method for soils in which the fluorine is finally determined by the colorimetric ferric thiocyanate method of Foster (28). A similar method has been used by McHargue (34).

Following Snell's procedure for fusion and extraction of the sample, the modified Armstrong method was applied. Trouble was encountered from gelatinous silica which prevents distillation of the fluorine. Results on a number of soils gave a maximum of 0.02% fluorine, but checks could not be obtained. Precipitation of the aluminum and silica with ammonium carbonate gave rather lower results as might be expected, since aluminum hydroxide adsorbs very considerable amounts of fluoride. Extraction of the residue left by the evaporation of the hot-water extract with 50% ethanol gave lower results still, although later evidence indicates that these values were fairly accurate.

Extraction of the fusion mixture with alcohol gave very low results.

A method was finally adopted which theoretically ought to give accurate values for fluorine content in



rocks and soils in which less than 0.1% of fluorine is present. Actually, fairly consistent results were obtained by this method on five soils in which the fluorine content was found to be less than 0.1% according to this method. No other method suggested would seem to give accurate values in this range, which incidentally seems to include most Alberta soils.

The procedure is as follows:

Fuse a one-gram sample of the soil in a platinum crucible with 4 gm. of a mixture of sodium carbonate and potassium carbonate (equal parts). After cooling, extract the melt with 60 c.c. hot water, filter and wash with four successive 10 c.c. portions of hot water. To the filtered extract add phenolphthalein and just discharge the color by slowly adding 6N sulfuric acid. Allow to stand over night. A gelatinous precipitate, largely silica, forms. This is filtered off and thoroughly washed with distilled water, the washings being added to the filtrate. The precipitate is placed in a large beaker, covered with 500 c.c. distilled water, stirred vigorously and allowed to stand over night. A portion of the supernatant liquid is analysed for fluorine by the Sanchis method, and the amount of fluorine so found is added to that to be determined in the filtrate.

The filtrate is made alkaline to phenolphthalein, concentrated to 50 c.c. and distilled with perchloric acid, according to the modified Armstrong procedure. The fluorine in the distillate is estimated by titration in



aqueous solution. Adding to this the fluorine dragged down by the gelatinous silica precipitate, one obtains the total fluorine content of the soil.

The method described above gives total fluorine. Practically, the acid-soluble fluorine is of more importance. This may be determined by direct distillation of the soil with perchloric acid (36) and subsequent titration by the Armstrong method. The value obtained represents the fluorapatite and fluorite present.



Distribution of Fluoride in Alberta Water

In the light of observations as to the effect of sulfates on the Sanchis method, some of the values previously obtained should be revised. Fortunately, the previous workers checked all results over 2 p.p.m. by the distillation method and such values are fairly reliable. Values between 1.0 and 1.2 for shallow wells may be eliminated as having no significance since a probable value for the sulfate correction would reduce them below the threshold value. Also on the basis of sulfate corrections, Barons can be removed from the list of places in which it is likely that mottled enamel may be found.

In the work done this year the following towns or districts have been added to the list of those in which a fluoride concentration greater than 1.0 p.p.m. has been found in one or more wells: Alix, Brant, Calgary, Cayley, Champion, Clyde, Edmonton, Irricana, Midnapore, Mountain View, Nanton, Parkland and Vimy. These places are all on the fringes of previously defined endemic areas (11).

Fluoride analyses of water from west of Wetaskiwin correlate with the presence of mottled enamel previously reported there. The affected area must be quite limited as analyses of water from surrounding districts show low fluoride content. The centre appears to be six miles west and three miles north of Wetaskiwin.



The Harris well at Gwynne produces the same type of water as the wells in the endemic area and probably taps the same aquifer. In respect to fluorine content it differs from all the neighboring wells (58).

Harris observed fluoride content over 1 p.p.m. in waters from Kirkcaldy, Vulcan, Lethbridge, Claresholm, Lacombe, Innisfail, Stavely, five samples from Olds, Benalto and Beaverlodge. The sample from Beaverlodge contained 3.0 p.p.m. of fluorides.

Information has been collected during the year indicating cases of mottled enamel arising from water at Aldersyde, Brant, Cayley and Nanton. Reports have also been received of the occurrence of mottled teeth in the Blindman river valley and in the district surrounding Beaverlodge.

The actual number of reports of dental fluorosis is much lower than might be expected from the results of water analyses. There must be a considerable number of cases which have not been reported or observed. Possibly the wandering habits of renters in the southern endemic districts may in part explain the low incidence. Another factor which must be considered is the increased use of deep-well sources as a community becomes older and more settled. The results of this, of course, will not appear until 6-12 years after such sources are tapped. In view of this the number of cases of mottled teeth in certain districts may be expected to show a marked increase in future.



The results of the analyses made this year which showed more than 1 p.p.m. of fluorine by either method employed are included in Table III. In Table IV are classified the results for streams, springs and lakes. The fluoride content is low in every case. Willow creek, (Claresholm), is interesting in that it shows the highest value for any stream and a much higher ratio of fluoride to total solids than many well waters. Its location in an endemic district is therefore significant. Lees Creek in Cardston must be the cause of cases of mottled enamel observed there, but analyses made on this water show a low fluoride content. It is just possible that this may be due to the presence of phosphates. On the other hand, it may be due to seasonal variations as has been suggested (11).

Considering the sources of the water-supplies in the endemic area in south-western Alberta, we have first Calgary and Lethbridge which are supplied by river-water low in fluorine. Similarly the towns and villages of Okotoks, Turner Valley, High River, Carmangay and Macleod, are supplied largely by rivers. Claresholm town supply is pumped from Willow Creek and the Cardston supply is obtained from Lees Creek.

Barons water comes almost entirely from wells supplied by seepage from the Lethbridge Northern irrigation ditch a mile south of town. No serious amount of fluorine is present. Picture Butte, Raymond and Brooks have reservoirs supplied by irrigation water. Indeed, all through the



Table III

| Lab No. | Place                                       | Depth | pH <sup>+</sup> | Results of Analysis in p.p.m. F <sup>-</sup> |                      |                   |                |
|---------|---------------------------------------------|-------|-----------------|----------------------------------------------|----------------------|-------------------|----------------|
|         |                                             |       |                 | Sanchis                                      | Armstrong            | Sanchis Corrected | Accepted Value |
| 387     | Kathryn                                     | 60'   | 8.9             | >4                                           | 5.2                  |                   | 5.2            |
| 402     | Olds                                        | 375   | ---             | 2.2                                          | 2.1                  |                   | 2.1            |
| 411     | Champion                                    | 180   | 8.8             | {2.4<br>2.4}                                 | {1.9<br>1.9}         | 1.9               | 1.9            |
| 422     | Calgary                                     | 85    | 8.7             | >3                                           | 4.8                  |                   | 4.8            |
| 451     | Strathmore                                  | 150   | 8.3             | >1                                           | 1.4                  |                   | 1.4            |
| 458     | Claresholm                                  | nil   | 8.45            | >1.2                                         | {0.5<br>0.3}         | >0.2              | 0.4            |
| 476     | Vimy                                        | 180   | 8.7             | >1                                           | {1.5<br>0.8?<br>1.5} |                   | 1.5            |
| 478     | Ponoka                                      | --    | 8.8             | 0.9<br>0.9                                   | 2.2                  | 0.9               | 0.9            |
| 485     | Killam                                      | --    | 8.0             | >1.0                                         | 0.3                  | >0.0              | 0.3            |
| 489     | Cochrane                                    | 46    | 8.6             | 1.0                                          | 0.7                  | 0.9               | 0.8            |
| 497     | Champion                                    | --    | 8.5             | >1                                           | 1.4                  |                   | 1.4            |
| 520     | Fleet                                       | 45    | 7.9             | >1                                           | {1.3<br>1.5}         |                   | 1.4            |
| 525     | Huxley<br>(7600 p.p.m.<br>SO <sub>4</sub> ) | 18    | 8.1             | >1                                           | {0.7<br>0.7}         |                   | 0.7            |
| 528     | Halkirk                                     | 280   | 8.3             | >1<br><2                                     |                      |                   | 1.5            |
| 529     | Irricana                                    | 22    | 8.2             | >1                                           | 2.3                  |                   | 2.3            |
| 537     | Calgary                                     | --    | 8.7             | >1                                           | 0.6                  | 0.6 or +          | 0.6            |
| 541     | Wetaskiwin NW                               | 150   | 9.2             | 1.0<br>1.0                                   | 0.7                  |                   | 0.7            |
| 542     | Wetaskiwin NW                               | 150   | 9.15            | >1.5                                         | 2.6                  |                   | 2.6            |
| 543     | Wetaskiwin                                  | 260   | 9.1             | >1.5                                         | 1.8                  |                   | 1.8*           |
| 544     | Wetaskiwin W                                | 360   | 9.2             | >1.2                                         | 1.8                  |                   | 1.8            |
| 545     | Wetaskiwin W                                | 277   | 8.3             | >1.2                                         | 2.0                  |                   | 2.0            |



Table III (cont'd.)

| Lab No. | Place         | Depth | pH <sup>+</sup> | Results of Analysis in p.p.m. F <sup>-</sup> |                     |                   |                |
|---------|---------------|-------|-----------------|----------------------------------------------|---------------------|-------------------|----------------|
|         |               |       |                 | Sanchis                                      | Armstrong           | Sanchis Corrected | Accepted Value |
| 546     | Wetaskiwin NW | 200'  | 8.4             | 1.0                                          | 1.0                 |                   | 1.0            |
| 550     | Olds          | 260   | 8.5             | 2.0                                          | 1.9                 |                   | 1.9            |
| 571     | Macleod       | 80    | 8.7             | 3.7                                          | 2.4 }<br>2.3 }      | 3.7               | 2.4            |
| 576     | Vimy          | 200   | 8.4             | 1.2                                          | 0.8                 |                   | 0.8            |
| 589     | Vegreville    | --    | 7.65            | 1.2                                          | 0.2                 | 0.0               | 0.2            |
| 607     | N. Edmonton   | 280   | 8.05            | 0.9                                          | 0.8 }<br>0.9 }      |                   | 0.9            |
| 615     | Edmonton      | 288   | 8.2             | 0.7                                          | 1.2                 | 0.5               | 1.2            |
| 620     | Brant         | 169   | 8.35            | 4.2                                          | 4.3                 | 4.1               | 4.2            |
| 642     | Mountain View | 15    | 7.7             | >1.4                                         | 2.3 }<br>0.5? }     | >1.4              | 2.3            |
| 644     | Cummings      |       | 7.6             | 1.4                                          | 1.5 }<br>0.2? }     | 1.4               | 1.4            |
| 645     | Wrentham      | 150   | 8.1             | 1.5                                          | 0.3 }<br>0.2 }      | 1.1               | 0.3            |
| 646     | Kitscoty      | --    | 7.3             | 1.5                                          | 0.9 }<br>? }<br>? } | 1.3               | 1.3            |
| 647     | Waskatenau    | --    | 8.2             | 1.2                                          | 0.5                 | 1.0               | 0.5            |
| 650     | Barons        | 93    | 7.4             | 1.8                                          | 0.5                 | 0.0               | 0.5            |
| 663     | Acme          | --    | 8.3             | 0.9                                          | 0.9 }<br>1.1 }      | 0.6               | 1.0            |
| 666     | Midnapore     | 190   | 9.1             | 2.0                                          | 2.6                 |                   | 2.6            |
| 667     | Cowley        | --    | 8.9             | 1.4                                          | 1.2                 |                   | 1.2            |
| 676     | Nanton        | 100   | 8.8             | 3.0                                          | 3.3                 |                   | 3.3            |
| 678     | Cheadle       | 94    | 7.8             | 1.0                                          | 0.9 }<br>0.9 }      |                   | 0.9            |
| 680     | MacLennan     | --    | 7.3             | 0.6                                          | 0.1                 | 0                 | 0.0            |
| 684     | Nanton        | 153   | 8.35            | 1.8<br>2.0                                   | 1.1 }<br>1.0 }      | 1.2<br>1.4        | 1.1            |



Table III (cont'd.)

| Lab<br>No. | Place                                | Depth            | pH <sup>+</sup> | Results of Analysis in p.p.m. F <sup>-</sup> |                         |                   |                |
|------------|--------------------------------------|------------------|-----------------|----------------------------------------------|-------------------------|-------------------|----------------|
|            |                                      |                  |                 | Sanchis                                      | Armstrong               | Sanchis Corrected | Accepted Value |
| 685        | Alston<br>(Vulcan)                   | 150'             | 7.8             | 2.0<br>2.0                                   | 1.5 }<br>1.6 }          | 1.8<br>1.8        | 1.6*           |
| 688        | Purple<br>Springs                    | 12               | 8.35            | 1.0                                          | 1.7 }<br>1.0 }          |                   | 1.0            |
| 691        | Red Deer                             | 130              | 8.85            | 3 app.                                       | 2.2 }<br>2.2 }          |                   | 2.2            |
| 694        | Granum                               | --               | 7.9             | 1.4                                          | 0.6 }<br>0.7 }          |                   | 0.7            |
| 695        | Kingman                              | --               | 7.5             | 0.9                                          | 0.3                     | 0                 | 0.3            |
| 696        | Banff                                | Sulfur<br>Spring | 7.8             | 0.9                                          | 1.1 }<br>1.4 }          |                   | 1.1            |
| 698        | Clyde                                | 100              | 8.7             | 1.8<br>1.8                                   | 1.5 }<br>2.7 }<br>2.1 } |                   | 1.8            |
| 700        | Winterburn                           | 384              | 8.55            | 2.4                                          | 2.7                     |                   | 2.5            |
| 701        | Winterburn                           | 250              | 8.65            | 2.1                                          | 1.6                     |                   | 1.6            |
| 702        | Brant                                | 160              | 8.8             | 4.2<br>4.5                                   | 4.6<br>5.8              | 4.2<br>4.5        | 4.6*           |
| 703        | Brant                                | 160              | 8.8             | 1.8                                          | 1.5                     | 1.7               | 1.6            |
| 704        | Brant                                | 138              | 8.8             | 2.4                                          | 2.7                     | 2.3               | 2.5            |
| 710        | Holden                               | --               | 8.2             | 0.8                                          | 1.0 }<br>1.0 }          |                   | 1.0            |
| 711        | Cayley                               | --               | 8.5             | >2.5                                         | 4.2<br>4.5              | >2.5              | 4.3            |
| 712        | Cayley                               | --               | 8.3             | 1.7                                          | 1.4                     | 1.2               | 1.3            |
| 714        | Nampa                                | --               | 5.4             | no t<br>result                               | 1.4                     |                   | 1.4            |
| 716        | Parkland<br>(sec. 19<br>Tp.15 R27W4) | 147              | 8.4             | 2.1<br>2.2                                   | 1.8                     |                   | 1.8            |
| 717        | Nanton                               | 110              | 8.3             | 3.6                                          | 3.0                     |                   | 3.0            |
| 718        | Nanton                               | 82               | 8.3             | 0.8                                          | 1.0                     |                   | 1.0            |



Table III (cont'd.)

| Lab<br>No. | Place               | Depth                            | pH <sup>+</sup> | Results of Analysis in p.p.m. F <sup>-</sup> |              |                   |                |
|------------|---------------------|----------------------------------|-----------------|----------------------------------------------|--------------|-------------------|----------------|
|            |                     |                                  |                 | Sanchis                                      | Armstrong    | Sanchis Corrected | Accepted Value |
| 720        | Parkland            | 210'                             | 8.5             | 2.7                                          | 2.7          | 2.7               | 2.7            |
| 723        | Critchley           | 119                              | 7.3             | 0.4?                                         | 1.8          |                   | 1.8            |
| 724        | Markerville         | 22                               | 7.3             | no<br>result                                 | 1.2<br>1.1   |                   | 1.1            |
| 728        | Fleet               | --                               | --              | 1.1                                          | 0.2          | 0.2               | 0.2            |
| 729        | Manyberries         | Artesian<br>Milk R.<br>Sandstone | 8.75            | 1.2<br>1.2                                   | ?<br>?       | 1.2<br>1.2        | 1.2<br>1.2     |
| 733        | Eyremore            | 8                                | 7.85            | >1.5                                         | 1.1<br>2.5   |                   | 1.1            |
| 735        | Didsbury            | --                               | 7.65            | no<br>result                                 | 2.0<br>2.1   |                   | 2.0            |
| 738        | Claresholm          | Willow<br>Creek                  | 8.2             | 0.7                                          | ?            | 0.7               |                |
| 739        | Granum              | --                               | 8.55            | 4.2                                          | 4.6          | 4.1               | 4.4            |
| 743        | Alix                | 200                              | 8.45            | 0.9<br>1.0                                   | 2.2?<br>3.0? |                   | 1.0            |
| 748        | Grande<br>Prairie   | --                               | --              | 1.0                                          | 2.3?<br>3.5? |                   | 1.0            |
| 755        | Alix                | 160                              |                 | 1.4                                          | 1.7          |                   | 1.4            |
| 757        | Ghost Pine<br>Creek | --                               | --              | 0.8<br>0.8                                   | 2.6          |                   | 0.8            |
| 761        | Blackie             | --                               | --              | 1.0<br>0.9                                   |              |                   | 1.0            |
| 767        | Chipman             | 250                              |                 | 0.7                                          | 1.2          |                   | 1.2            |
| 770        | Raymond S.          |                                  |                 | 1.4<br>1.2                                   |              | 1.0               | 1.0            |
| 783        | Halcourt            | 250                              |                 | 1.8                                          |              | 1.7               | 1.7            |



Table IV

| <u>Streams</u>          |            |                | <u>Springs</u>    |              |                 |                |
|-------------------------|------------|----------------|-------------------|--------------|-----------------|----------------|
| Place                   | Lab<br>No. | F <sup>-</sup> | Place             | Lab<br>No.   | pH <sup>+</sup> | F <sup>-</sup> |
| Edmonton                | 226        | 0.05           | Donalda           | 49           |                 | 0.6            |
|                         | 416        | 0.2            | Westlock          | 6            |                 | 0.5            |
| Nordegg                 | 140        | 0.2            | Banff             | 64           |                 | 0.9            |
| Tawatinaw               | 161        | 0.4            |                   | 696          | 7.8             | 1.1            |
| Red Deer                | 76         | 0.1            |                   | 697          | 7.9             | 0.6            |
| Banff                   | 65         | 0.1            | Hill Spring       | 214          |                 | 0.8            |
| Calgary                 | 21         | 0.3            | Walsh             | 100          |                 | 0.1            |
|                         | 46         | 0.3            | Picture Butte     | 81           |                 | 1.0            |
| Blairmore               | 112        | 0.05           |                   | 101          |                 | 0.0            |
| Drumheller              | 110        | 0.1            | Taber             | 86           |                 | 0.5            |
| Medicine Hat            | 41         | 0.2            | Yankee Valley     | 604          | 7.55            | 0.05           |
|                         | 595        | 0.0            | Cheadle           | 679          | 7.8             | 0.3            |
| Okotoks                 | 127        | 0.5            | Manyberries       | 729          | 8.75            | 1.2            |
| Turner Valley           | 70         | 0.2            | Bilby             | 483          |                 | 0.1            |
|                         | 210        | 0.3            | Whitemud          | 452          |                 | 0.4            |
|                         | 320        | 0.2            |                   |              |                 |                |
|                         | 390        | 0.35           |                   |              |                 |                |
| Cardston                | 15         | 0.0            |                   |              |                 |                |
|                         | 114        | 0.1            |                   |              |                 |                |
|                         | 195        | 0.25           |                   |              |                 |                |
|                         |            |                |                   | <u>Lakes</u> |                 |                |
|                         |            |                | Place             | Lab<br>No.   | pH <sup>+</sup> | F <sup>-</sup> |
| Picture Butte Reservoir | 147        | 0.5            | Cousins           | 209          |                 | 0.7            |
| Coalspur                | 278        | 0.2            | Jasper            | 213          |                 | 0.05           |
| Mt. Park                | 396        | 0.35           | St. Paul          | 438          | 8.9             | 0.3            |
| High River              | 400        | 0.4            | Lesser Slave Lake | 491          |                 | 0.1            |
| Whitemud                | 454        | 0.5            | Lac La Biche      | 500          |                 | 0.1            |
|                         | 524        | 0.2            |                   |              |                 |                |
| Claresholm              | 738        | 0.7            | Cold Lake         | 628          | 8.1             | 0.0            |



irrigation districts, the main source of supply is the ditch which is used to supply either reservoirs or seepage wells. On the three Indian reserves (approximately 32 townships) surface supplies are used to a large extent.

By far the largest number of waters high in fluorine come from deep wells, although by no means all such are affected. In those cases in which shallow wells (see Table V) show an appreciable fluorine content, they appear to have reached a rock formation. Artesian wells frequently show high fluorine content. In the southern part of the province the Milk River sandstone has been identified as the aquifer supplying such wells.

In view of the effect of phosphates on the Sanchis method, it seemed desirable to have some idea of the concentration of phosphates likely to be met with in natural waters. No information was available so a number of analyses were made using the method of Scott (40) and the results are given in Table VI.

The complete analyses of certain typical waters containing fluorine are given in Table VII.

The results of the surveys to date are summarized on the accompanying maps.

Comparison of these maps with the geological survey map published by Dr. John Allan in 1937 for the Research Council of Alberta indicates that the more serious cases of mottling are all to be found in the area classified on the geological map as Paskapoo or Willow Creek formation. A considerable number of the mild cases are found in the



Table V

Shallow wells (less than 60 feet in depth) which show a fluoride content over 1 p.p.m.

| <u>Lab. No.</u> | <u>Place</u>   | <u>Depth</u> | <u>F</u> |
|-----------------|----------------|--------------|----------|
| 13              | Shepard        | 30'          | 1.4      |
| 61              | Stettler       | 30           | 1.1      |
| 91              | Whitelaw       | 40           | 1.1      |
| 148             | Picture Butte  | 15           | 1.4      |
| 163             | Olds           | 32           | 2.0      |
| 193             | New Dayton     | 6            | 1.2      |
| 197             | Beynon         | 26           | 1.0      |
| 223             | Beynon         | 24           | 1.0      |
| 520             | Fleet          | 45           | 1.4      |
| 529             | Irricana       | 22           | 2.3      |
| 642             | Mountain View  | 15           | 2.3      |
| 688             | Purple Springs | 12           | 1.0      |
| 724             | Markerville    | 22           | 1.1      |
| 733             | Eyremore       | 8            | 1.1      |

Analyses up to and including No. 223 have been previously reported (11). These values were not corrected for sulfates, while the remaining six have been.



Table VIPhosphates in Natural Waters

| <u>Lab. No.</u> | <u>Place</u> | <u>Depth</u> | <u>P<sub>2</sub>O<sub>5</sub> in p.p.m.</u> |
|-----------------|--------------|--------------|---------------------------------------------|
| 324             | Wetaskiwin   | 146'         | 4                                           |
| 476             | Vimy         | 180          | 3.5                                         |
| 572             | Calgary      | --           | 14                                          |
| 573             | Bentley      | 40           | 2                                           |
| 574             | Lac la Biche | 67           | 8                                           |
| 575             | Barrhead     | 105          | 3                                           |
| 576             | Vimy         | 200          | 3                                           |
| 577             | Vimy         | 15           | 10                                          |
| 578             | Vimy         | 20           | 12                                          |
| 579             | Three Hills  | --           | 15                                          |
| 580             | Calgary      | 114          | 18                                          |
| 581             | Holden       | --           | 20                                          |
| 582             | Andrew       | 14           | <3 (off.)                                   |
| 586             | Lloydminster | --           | 0                                           |
| 698             | Clyde        | 100          | 0.5                                         |
| 704             | Brant        | 160          | 0                                           |
| 711             | Cayley       | --           | 0                                           |
| 720             | Parkland     | 210          | 0                                           |
| 739             | Granum       | --           | 0.5                                         |

Phosphates in Treated Waters

|                | <u>Sample</u>       | <u>P<sub>2</sub>O<sub>5</sub> in p.p.m.</u> |
|----------------|---------------------|---------------------------------------------|
| <u>Harris:</u> | Effluent @ 200 gal. | 15                                          |
|                | @ 600 gal.          | 4                                           |
|                | @ 1000 gal.         | 3                                           |
| <u>Henker:</u> | Effluent @ 250 gal. | 12                                          |
|                | @ 350 gal.          | 30                                          |
|                | @ 450 gal.          | 7                                           |



Table VII

Water Analyses

|                                  | #411<br>Champion | Edmonton<br>City | #715<br>Gwynne | #684<br>Nanton | #720<br>Parkland | #739<br>Granum |
|----------------------------------|------------------|------------------|----------------|----------------|------------------|----------------|
| Total Solids<br>@ 105° C.        | 1822             | 199              | 964            | 4496           | 1032             | 1128           |
| Loss on Ign.                     | 80               | --               | 212            | 200            | 200              | 136            |
| SO <sub>4</sub> <sup>=</sup>     | 1194             | 30               | 11             | 1800           | 95               | 342            |
| Cl <sup>-</sup>                  | 77               | 4                | 70             | 27½            | 46               | 65             |
| Bicarbonate<br>Alkalinity        | 295              | 110              | 554            | 365            | 522              | 353            |
| Carbonate<br>Alkalinity          | --               | 0                | 69             | 26             | 25               | 28             |
| Hardness<br>as CaCO <sub>3</sub> | 20               | 152              | 0              | 125            | 16               | 22             |
| pH <sup>+</sup>                  | 8.8              | 8.2              | 9.3            | 8.35           | 8.5              | 8.55           |
| P <sub>2</sub> O <sub>5</sub>    | --               | --               | 4              | --             | 0                | 0.5            |
| F                                | 1.9              | 0.2              | 1.2            | 1.0            | 2.7              | 4.4            |

All results expressed as p.p.m.

Analysis of #411 was obtained from the  
Provincial Laboratory.



# ALBERTA

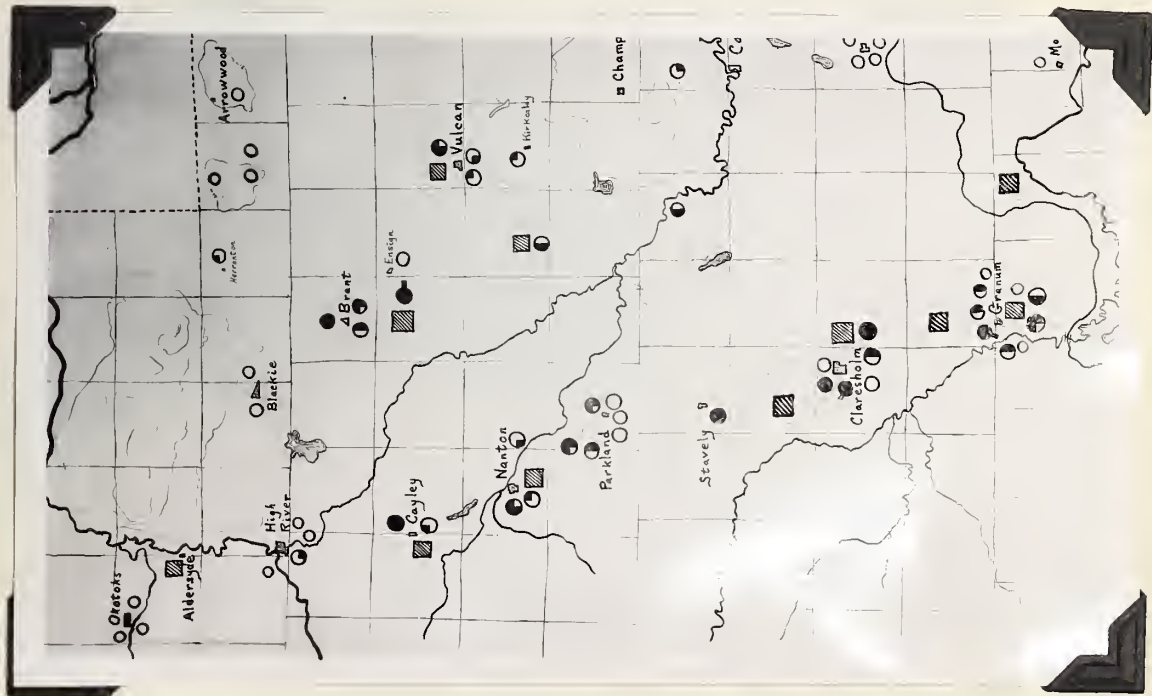
X = Cases of Mottled Teeth.

• = Fluorine Content of one or more Samples of Water greater than 1 p.p.m.



Map No. 1



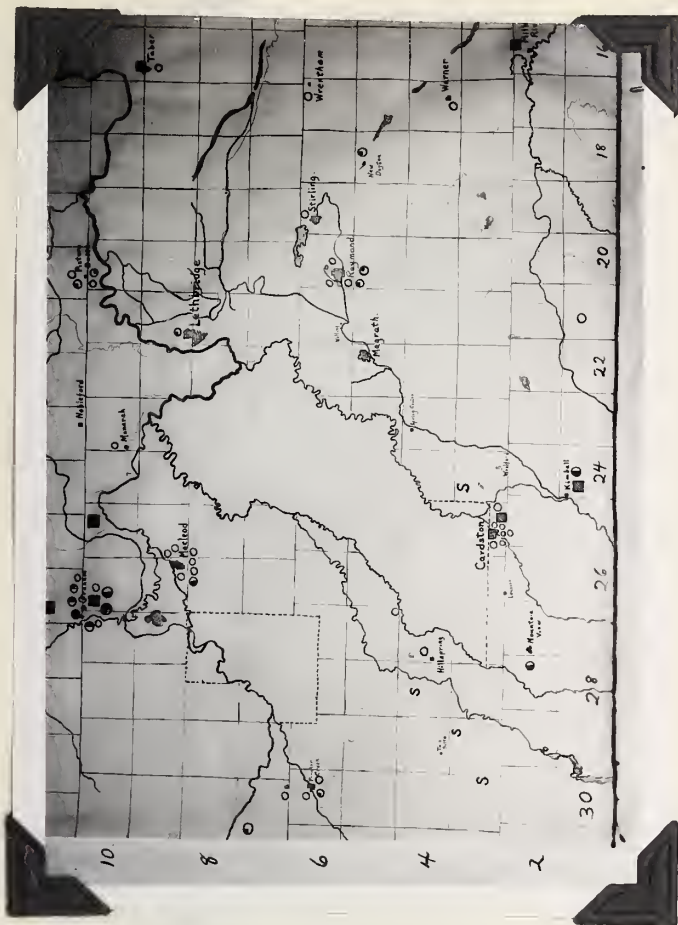


No. 2

Claresholm

and

District



No. 3 Cardston and District

Key

|                                   |   |
|-----------------------------------|---|
| Cases of Mottled Teeth            | ▨ |
| Water less than 1 p.p.m. fluoride | ○ |
| 1.0 - 1.5 p.p.m.                  | ◐ |
| 1.5 - 2.5 p.p.m.                  | ◑ |
| 2.5 - 3.5 p.p.m.                  | ◒ |
| 3.5 - 4.5 p.p.m.                  | ◓ |
| 4.5 - 5.5 p.p.m.                  | ◔ |







division described as Belly River formation.

In considering the possible origin of fluorine in waters, we may first discuss the minerals. The minerals containing fluorine and the amounts found in them are:

|                |                 |
|----------------|-----------------|
| Biotite        | trace - 4.23% F |
| Muscovite      | 0.12 - 1.26%    |
| Lepidolite     | - 11%           |
| Phlogopite     | 0.82 - 5.67%    |
| Tourmaline     | 0.06 - 1.19%    |
| Fluorite       | - 48.9%         |
| Apatite        | 1.31 - 3.86%    |
| Phosphate rock | 0.4 - 6.0%      |

The first four of these are micas, which, along with the borosilicate, tourmaline, are widely distributed in soils and rocks. All of these, however, are very slightly soluble, if at all, and so are unlikely to be the cause of the presence of fluorine in water-supplies. The last three named minerals are appreciably soluble. Clark (1) states that percolating waters containing bicarbonates or carbonates attack fluorite, altering it to calcite and carry away the fluoride set free. Clark is also authority for the statement that fluorite occurs as a cementing material in certain sandstones, (a phosphatic brown sandstone at Kursk, Russia contained 2.4% fluorine.) Some soluble fluorine compound is also present in certain limestones (55, 58, 2).

The possibility of organic origin must also be considered. Fluorine is found in bones, tooth enamel, skin,



hair and blood so that we have a considerable source of this element in decaying animal matter. It is also found in plants, occurring largely in the roots, where it is apparently deposited as  $\text{CaF}_2$ . The abnormally high <sup>fluorine</sup> content of the sorrel (138.7 p.p.m. of fresh substance) (5) is interesting in that it presents the possibility of this plant being a fluoride-accumulator. The sour-dock, a member of the same botanical family, flourishes over large areas in southern Alberta, and it will be interesting to examine this plant for its fluorine content.

The results of the soil analyses which were carried out by the methods previously described are given in Table VIII. These soils were specially selected in that their content of phosphorus was much higher than usual. The samples were obtained from the Department of Soils which collected them in the course of soil surveys in different parts of the province. The locations from which the samples were obtained have been indicated on the map of the district by the letter S. (See map #3).

It was observed early in the survey this year that waters containing fluorides in any quantity were quite alkaline. pH determinations were therefore made on 236 samples of water employing the glass electrode, which is the only satisfactory method for the range required, (viz. 6.0 - 10.0) in such weakly buffered solutions as potable waters may be. The values found represent the pH of the sample after it has come to equilibrium with the air and may hence differ from the values obtained for



Table VIIIFluorine in Soils

| <u>Lab. No.</u> | <u>Location</u>   | <u>P</u> | <u>F</u> | <u>Average Value F</u> |
|-----------------|-------------------|----------|----------|------------------------|
| D791            | Parkbend          |          | 0.055%   |                        |
|                 | 32 - 3 - 29W4     | 0.118%   | 0.069    | 0.062%                 |
| D795            | Twin Butte        |          | 0.054    |                        |
|                 | 13 - 3 - 30W4     | 0.108    | 0.058    | 0.056                  |
| D811            | Hillspring        |          | 0.049    |                        |
|                 | 33 - 4 - 28W4     | 0.112    | 0.051    | 0.050                  |
| D886            | Raley             |          | 0.031    |                        |
|                 | 35 - 3 - 24W4     | 0.122    | 0.028    | 0.030                  |
| R494            | Dauphin, Manitoba |          | 0.048    |                        |
|                 |                   | 0.15     | 0.044    | 0.046                  |

Acid-Soluble Fluorine in soils

D795 --- 0.030%      single  
D811 --- 0.018%      determinations

The soil samples listed above and the phosphorus analyses were obtained through the courtesy of the Department of Soils.



freshly drawn samples, tending in general to be higher. It is nevertheless believed that most of them are significant. The values for the high-fluoride waters are given in Table III. Almost all of these values are plainly due to the alkali-carbonate -- bicarbonate buffer action (i.e. the pH is above 8.3). A notable exception is the acid water (#714) included, which contained a large amount of ferrous sulfate. The average pH of the 32 samples containing more than 1.5 p.p.m. fluorine is 8.53. These observations appear to be significant in relation to the previously mentioned power of attacking fluorite possessed by carbonate waters.

The pH of samples from 57 wells less than 60 feet deep was found to average 7.71.

Values less than pH 8.3 indicate the presence of free carbon dioxide or of calcium sulfate and magnesium sulfate which hydrolyse to give a slightly acid reaction. The majority of the samples from shallow wells, particularly in northern Alberta contain sulfates and show a comparatively low pH (less than 8.0). In general, a pH between 7.0 and 8.0 is to be associated with a well in the glacial drift.



### Removal of Fluorides from Water

Various workers have attempted to remove fluorides from water. Since no precipitant is available, recourse must be had to adsorption or to anion-exchange substances. Smith used ground bone (57) and found that the fluoride content of water which had passed through a column of this material was lowered. Activated carbon (54) is an efficient adsorbent if the pH of the water treated be less than 3, but this condition practically precludes its use. Fink and Lindsay employed activated alumina (50, 56) and Adler, Klein and Lindsay (45) introduced the use of tricalcium phosphate. Both of these materials have been marketed under the trade name, "Defluorite." They will be distinguished hereafter as defluorite A and defluorite B, respectively. These two materials may be regenerated after use. Regeneration has been performed by treatment with dilute sodium hydroxide, followed by treatment with dilute hydrochloric acid. Behrman and Gustafson (46) have improved the regeneration process in the case of defluorite B by substituting carbon dioxide solution for the hydrochloric acid. Elvove (49) has shown that magnesium oxide can be used in a very simple manner by stirring it up with the water to be treated and then allowing the suspension to settle out. Special procedures employing aluminum sulfate (51) and tricalcium orthophosphate (53) have recently been described. A blanket patent (48) has recently been taken out in Great Britain covering the use of a large group of metallic oxides as fluoride removers.



Harris (58) working in this laboratory has shown that heat treatment affects markedly the capacity of iron and aluminum oxides for fluoride adsorption. He found that air-dried alumina was, weight for weight, much superior to that dried at higher temperatures. Mole for mole, the air-dried material would still be more effective.

Elvove's procedure (49) has been adopted for the work in this laboratory as the one which might be most readily employed where required--i.e. on the farm or in a small town where the equipment available consists of a spoon and a bucket.

A preliminary test on alumina gave good results according to the following procedure. A weighed quantity of material was mixed thoroughly with a measured amount of water containing 4 p.p.m. fluoride. This water was made up by adding the calculated amount of C.P. sodium fluoride to Edmonton city water. A representative analysis of this water is given in Table VII. The mixture was allowed to stand over-night and the supernatant liquid was then siphoned off and analysed for fluorine content. The time of contact seems to be the controlling factor, rather than the amount or type of stirring so long as the substance becomes thoroughly wetted. The procedure was repeated in the case of each sample tested until the fluoride-removal capacity of the material had been reduced to well below a desirable amount.

Some of the materials tested were obtained from stock, others it was necessary to prepare. Analyses were



carried out on certain of the more efficient materials, as well as on one or two whose composition was doubtful.

The following materials possessed slight capacity to remove fluorides or else none at all: titanium oxide (stock), titanium hydroxide (prepared), zinc oxide (prepared), copper hydroxide (prepared), manganese dioxide (stock), hydrated manganese dioxide (48)(prepared), several samples of silica gel as prepared, bentonite (stock), zirconium silicate (stock), beryl (stock), ilmenite (stock), a limey sub-soil, copper sulfide (prepared), flowers of sulfur (stock), calcium oxalate (prepared), calcium oleate (prepared), trimagnesium orthophosphate (prepared), barium carbonate (prepared), barium sulfate (prepared), magnesium oxy-chloride (prepared), and chromium borate (48)(prepared). The amount of fluoride removed by any one of the above substances was insignificant.

In the case of several other materials, no conclusions could be drawn. Calcium hydrogen phosphate, when tested, dissolved to such an extent that analysis was made very difficult due to the interference of phosphates. In view of the fact that it was not practicable to use a substance so soluble, it was considered unnecessary to spend more time or trouble on this analysis. Similar difficulties were met with in the case of a resin, and this time no analytical results at all could be obtained. This resin, produced from m-phenylene-diamine and formaldehyde (52), is said to be an anion-exchange material with



a large capacity for sulfates. It was prepared by reducing m-nitroaniline with iron filings and hydrochloric acid, treating the product with concentrated hydrochloric acid to form the salt and then adding formaldehyde. Formalin solution was used as a source of formaldehyde. The jelly expected did not form but a gummy mixture was obtained. When this had been dried at  $110^{\circ}\text{C}$ , it was tested for fluoride-exchange capacity. Neither the Sanchis nor Armstrong methods gave any results. The water moreover acquired a disagreeable taste.

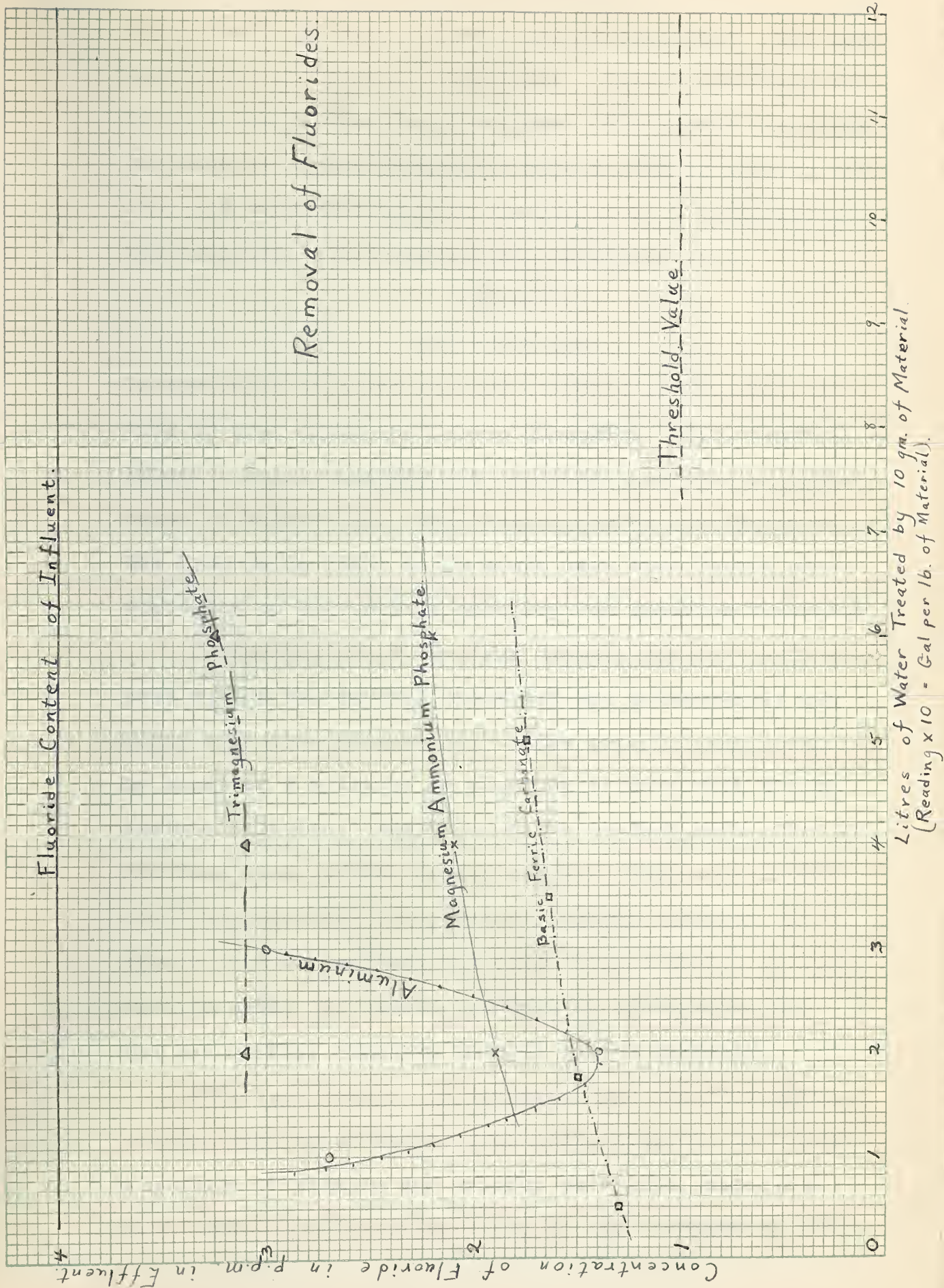
A number of materials showed a small capacity for fluorides: magnesium ammonium phosphate (prepared), basic iron carbonate (prepared) and powdered aluminum (stock). The results of the tests on these materials are shown in Figure II. The basic iron carbonate was prepared by neutralizing a solution of ferric chloride with a solution of sodium carbonate. The composition of the precipitate so obtained approximates to  $\text{Fe}(\text{OH})\text{CO}_3$  + water of hydration. The behavior of the powdered aluminum is to be expected since it exposes a large surface of the oxide. Unfortunately the capacity for adsorption has been lowered by changes in the structure of the oxide caused by the heat incidental to the pulverizing process.

Two attempts at preparation of ferric phosphate were made. In the first a solution of iron chloride was treated with a solution of disodium phosphate in excess. The product contained:

40.1%  $\text{P}_2\text{O}_5$   
and 6.1% Fe



Figure II.





which would indicate a ferric sodium phosphate. Its low solubility is somewhat surprising. This preparation was of no value in removing fluorides. The second preparation was made by adding phosphoric acid to ferric nitrate solution and neutralizing with ammonia until a precipitate was obtained. This precipitate consisted of :

48.5% Fe

and 25.5%  $P_2O_5$ .

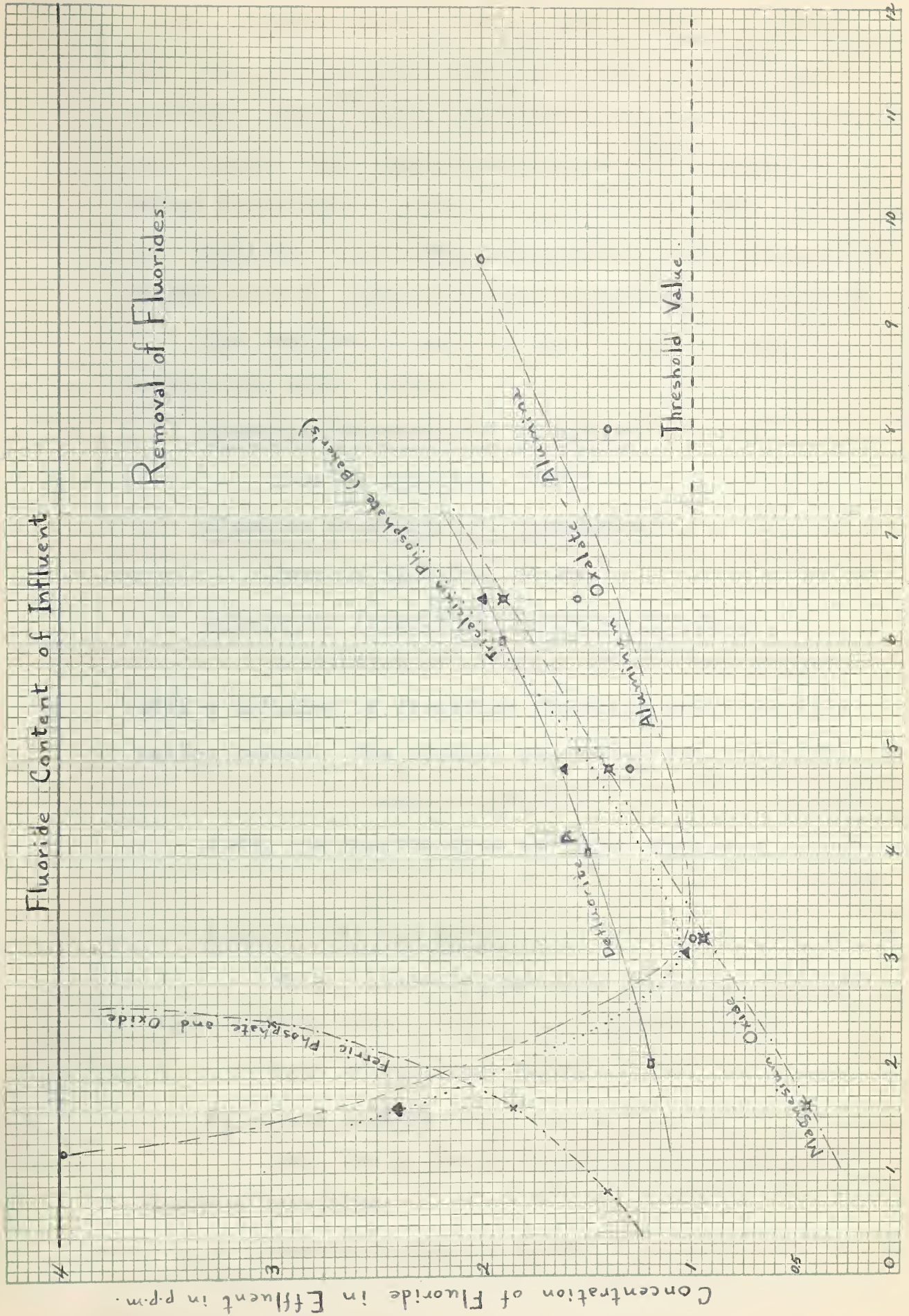
On the basis of these results it would seem to be a mixture of iron oxide and ferric phosphate. This material showed a small capacity for removing fluorides as indicated in Figure III. This action can be attributed to the iron oxide (58), so it would seem that ferric phosphate has no appreciable capacity for removing fluorides.

A preparation of aluminum oxalate removed no fluorides during the initial treatment but subsequently was quite effective (Figure III). The material was prepared by treating a solution of aluminum nitrate with sodium oxalate solution. Analysis of the product made after it had been used several times indicated that only 10.9% could be described as hydrated aluminum oxalate. If we assume that the surface was originally composed of the oxalate which hydrolysed, we have an explanation for the low initial capacity and its sudden increase.

Efficient removal of fluorides was observed with various samples of hydrated alumina, aluminum phosphate, a mixture of alumina and calcium carbonate, magnesium oxide and the defluorites A and B. The results of the



Figure III



Litres of Water Treated by 10 gm. of Material  
(Reading x 10 = Gal. per lb. of Material)



tests on these materials are given in Figures III and IV. The best material for the purpose is air-dried alumina, but air-dried aluminum phosphate is almost as efficient. The behavior of alumina with a synthetic water containing 8 p.p.m. of fluoride is shown in Figure V. (Synthetic water was prepared by adding the required amount of C.P. sodium fluoride to Edmonton city water).

The analyses of some of these fluoride removing agents are given below:

Aluminum Phosphate (J. T. Baker)

Loss on ignition 28.5%

Aluminum Phosphate (T. Schuchardt)

Loss on ignition 27.3%

Laboratory Preparation Aluminum Phosphate

A solution of aluminum nitrate was treated with a solution of di-sodium phosphate until precipitation ceased. The product was washed and air-dried.

Loss on ignition 45.9%

$\text{AlPO}_4$  (calculated from phosphate analysis) 46.3%

Total 92.2%

Alumina dried at 81° C.

This preparation was made by Harris (58) and dried for four hours @ 81° C. in a muffle furnace.

Loss on ignition 34.3%

Air-dried alumina

This was prepared from aluminum nitrate and ammonium hydroxide.

Loss on ignition 52.0%



Figure IV.

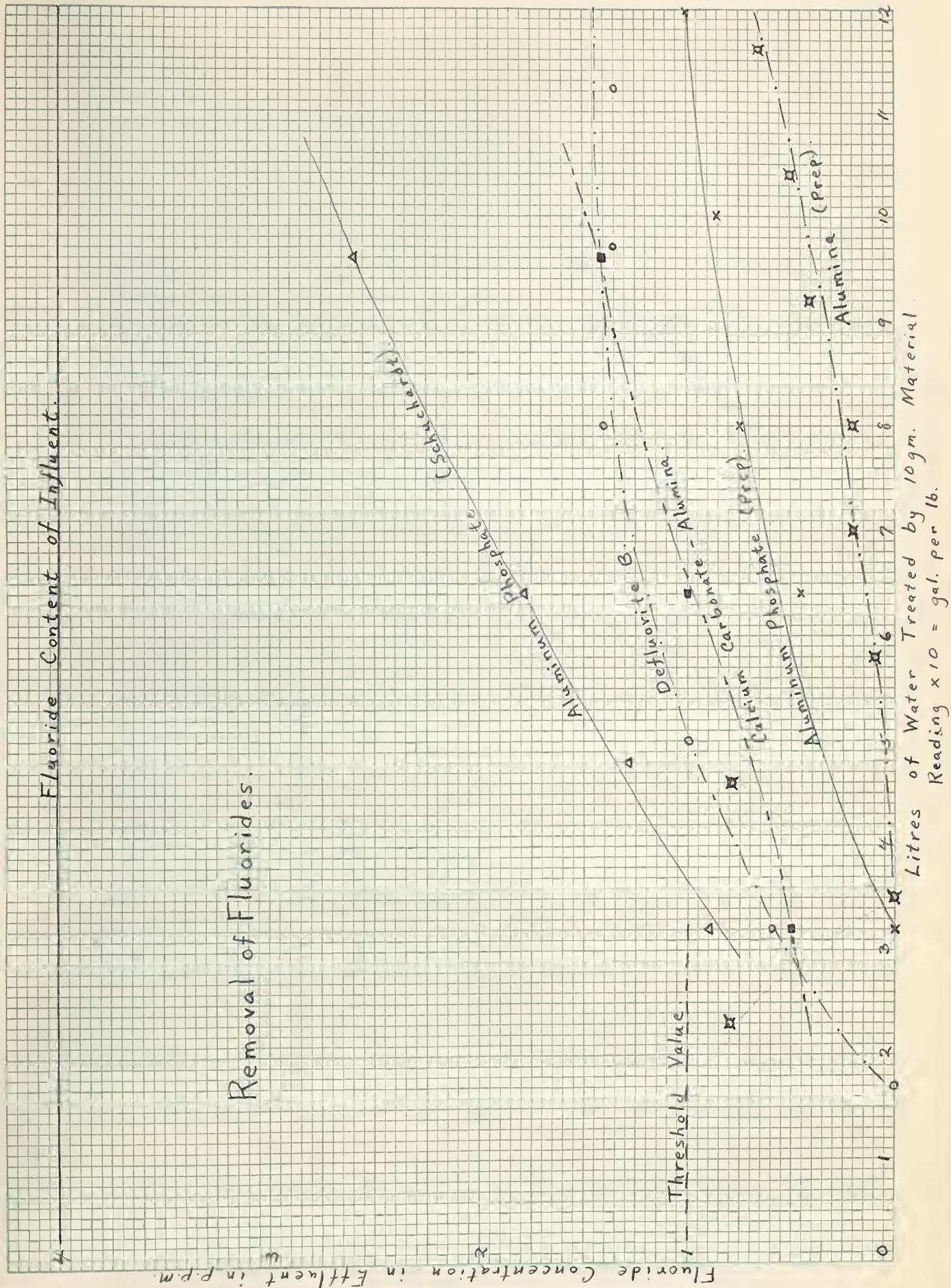
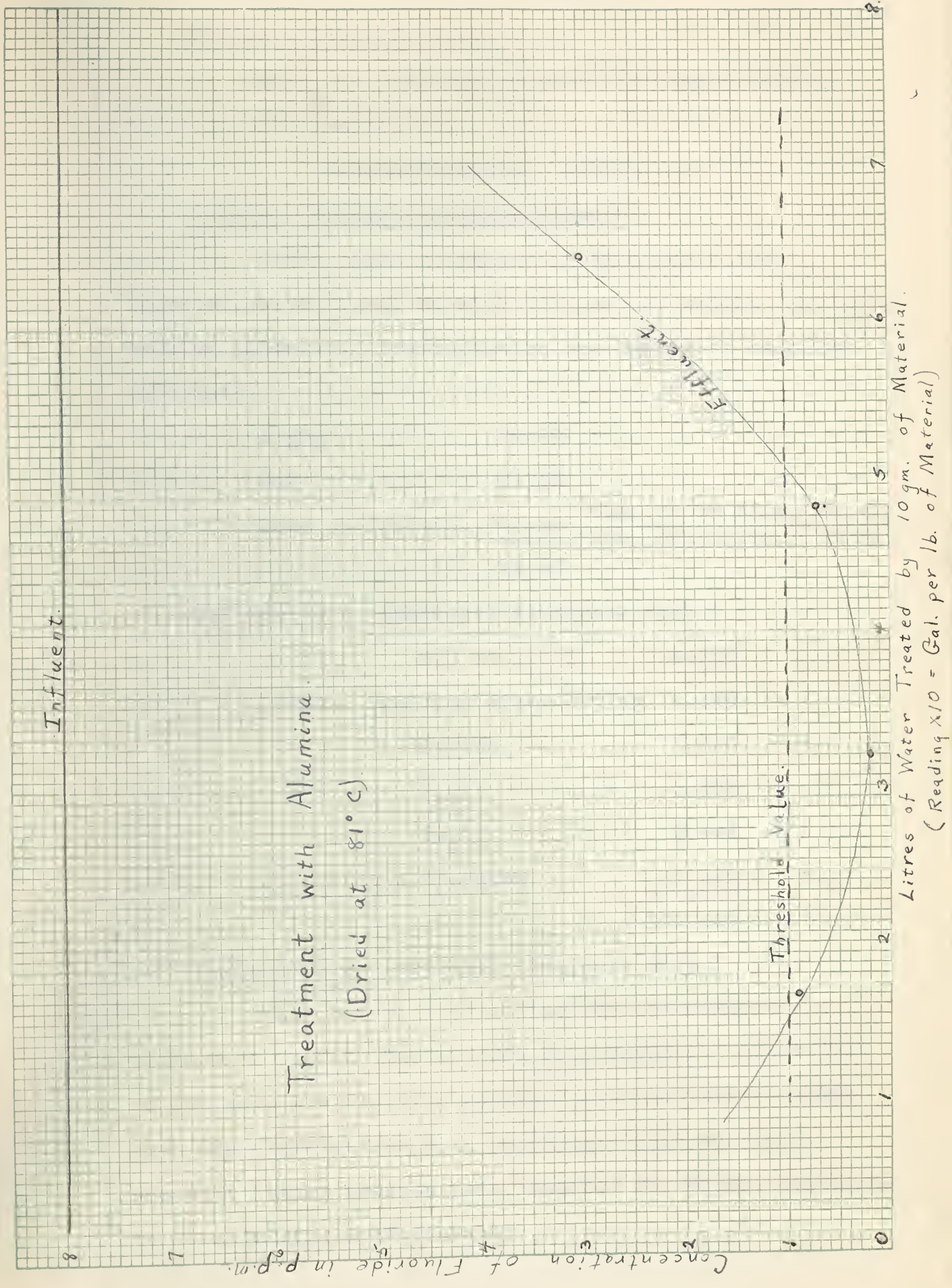




Figure V.





Ferric oxide (air-dried)

This was prepared by treating ferric nitrate solution with ammonia.

Loss on ignition 23.7%

Calcium Carbonate-Alumina Mixture

Three parts by weight of aluminum nitrate, hydrated, were dissolved with one part by weight anhydrous calcium chloride. Precipitation was made with ammonium carbonate.

|                         |              |                                   |       |
|-------------------------|--------------|-----------------------------------|-------|
| $\text{Al}_2\text{O}_3$ | 29.0%        |                                   |       |
| $\text{CaO}$            | 21.5%        |                                   |       |
| Loss on ignition        | <u>47.8%</u> | $\text{CO}_2$ (calculated)        | 16.9% |
|                         |              | $\text{H}_2\text{O}$ (calculated) | 30.9% |
|                         | 98.3%        |                                   |       |

Defluorite A (National Aluminate Corp.)

|                                               |               |
|-----------------------------------------------|---------------|
| $\text{H}_2\text{O}$ at $110^\circ\text{C}$ . | 4.35%         |
| Loss on ignition after drying                 | 6.69%         |
| Silica                                        | 2.64%         |
| $\text{P}_2\text{O}_5$                        | 3.40%         |
| $\text{Fe}_2\text{O}_3$                       | 2.04%         |
| $\text{Al}_2\text{O}_3$ (by difference)       | <u>81.32%</u> |
|                                               | 100.44%       |

Defluorite B (National Aluminate Corp.)

This material is defined by its makers as a mixture of  $\text{Ca}_3\text{P}_2\text{O}_8 \cdot \text{H}_2\text{O}$  and  $3\text{Ca}_3\text{P}_2\text{O}_8 \cdot \text{Ca}(\text{OH})_2$ . An attempt to estimate the fluorine content gave the value 0.008%, when one distillation with perchloric acid was made. Somewhat higher results were obtained for double distillations made with sulfuric acid.



In these analyses the loss on ignition may be taken as a measure of the water content of the sample, except where otherwise noted. Ignition was carried out at redness over a bunsen burner for 20 minutes in each case. This does not remove all of the water from hydrated alumina, but it does give a result which is sufficiently accurate for the purpose. (It may be noted that in determining the combined oxides in defluorite A, constant weight was obtained only after eight hours ignition over the blast lamp.) The water content, determined as above, is a measure of the porosity of the material and an indication of its structure. The effect of the moisture content on the fluoride removing capacity is clearly shown in Figure VI, in which the three samples of aluminum phosphate are compared on the basis of dry weight (i.e. moles of aluminum phosphate).

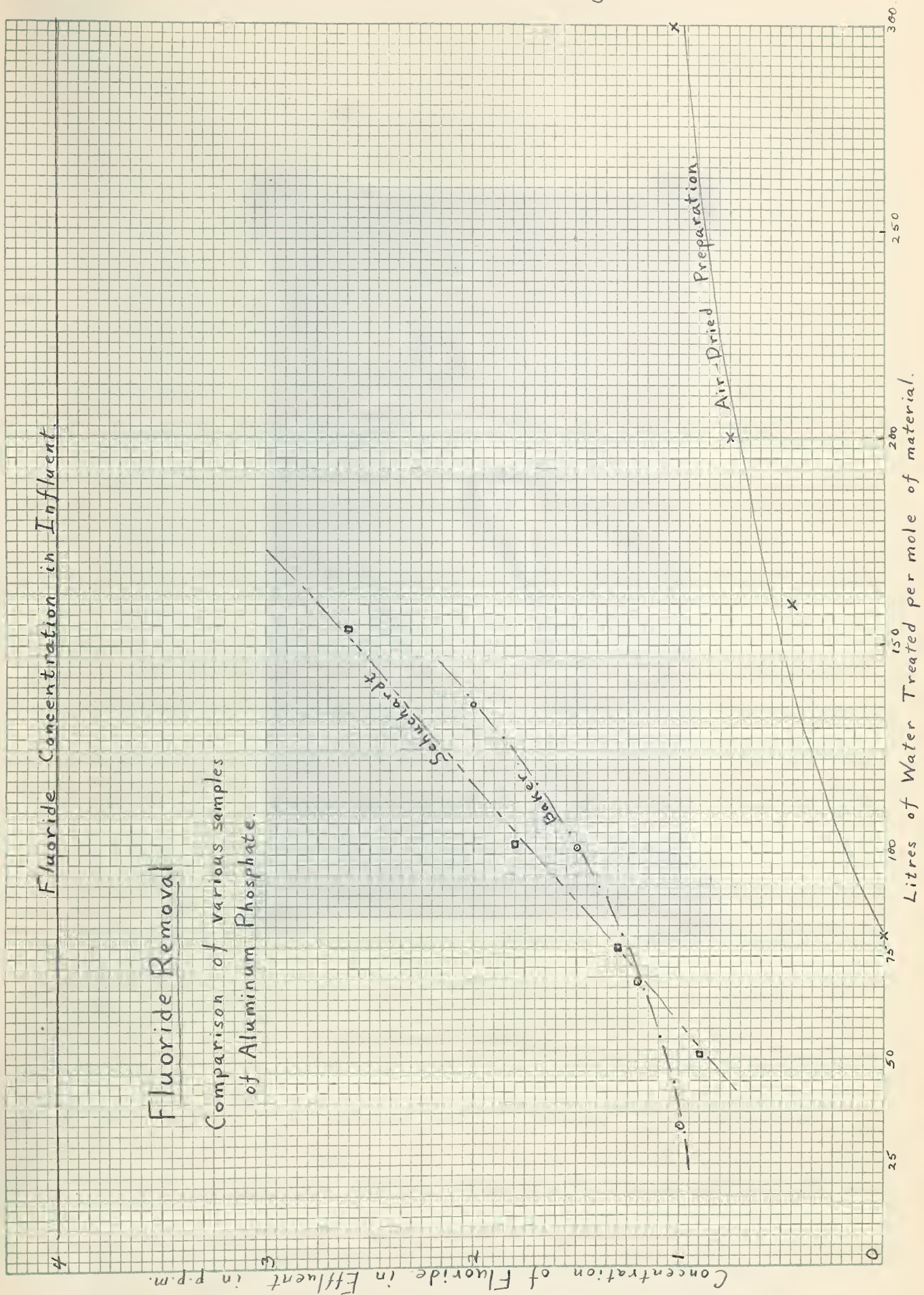
Two defluorite units were obtained from the National Aluminate Corporation. These units contain ten pounds of tricalcium phosphate (defluorite B). The unit itself has an inlet and an outlet designed to prevent clogging and is closed with a rubber seal cap which makes it airtight. The defluorite is in particles of 20 - 40 mesh size.

The unit is designed to operate under pressures up to 30 lbs. per sq. in., at a flow rate up to 3 gal. per min. It may be operated with gravity flow which gives a rate of approximately  $\frac{1}{2}$  gal. per min.

The unit is rated as having an initial capacity of treating 800 gallons of water containing 5 parts per



Figure VI.







DEFLUORITE UNIT



million of fluoride, so that the effluent contains less than one part per million.

One unit was employed at the Harris well near Gwynne, Alberta. The water was back washed through the unit at an average flow rate of three quarts per minute. The results of the operation are presented in Figure VIII. The effluent contains phosphates (see Table VI) and at some intervals was very cloudy. Determination of the residual fluorine had to be made by the Armstrong method using perchloric acid because of the interfering action of the phosphates. The mechanical operation was satisfactory, except that a momentary excess of pressure caused the bottom to spring and cracked the enamel. Some rusting occurred.

The removal of fluorides in this case was less than should be expected. This operation was possibly not a fair test in view of the low initial fluoride content of the water and its somewhat unusual nature (softness, lack of sulfates and pH of 9.3). The analysis of this water is given in Table VII as #715.

The second unit was operated at W. M. Henker's residence at Granum. The results are shown in Figure IX. An analysis of this water supply is presented in Table VII under #739. In this case the water was passed through more slowly, the unit being operated just as required for household purposes. Four hundred fifty gallons were drawn through the unit in about four weeks. The unit was then returned and has since been successfully regenerated.



Figure VII.

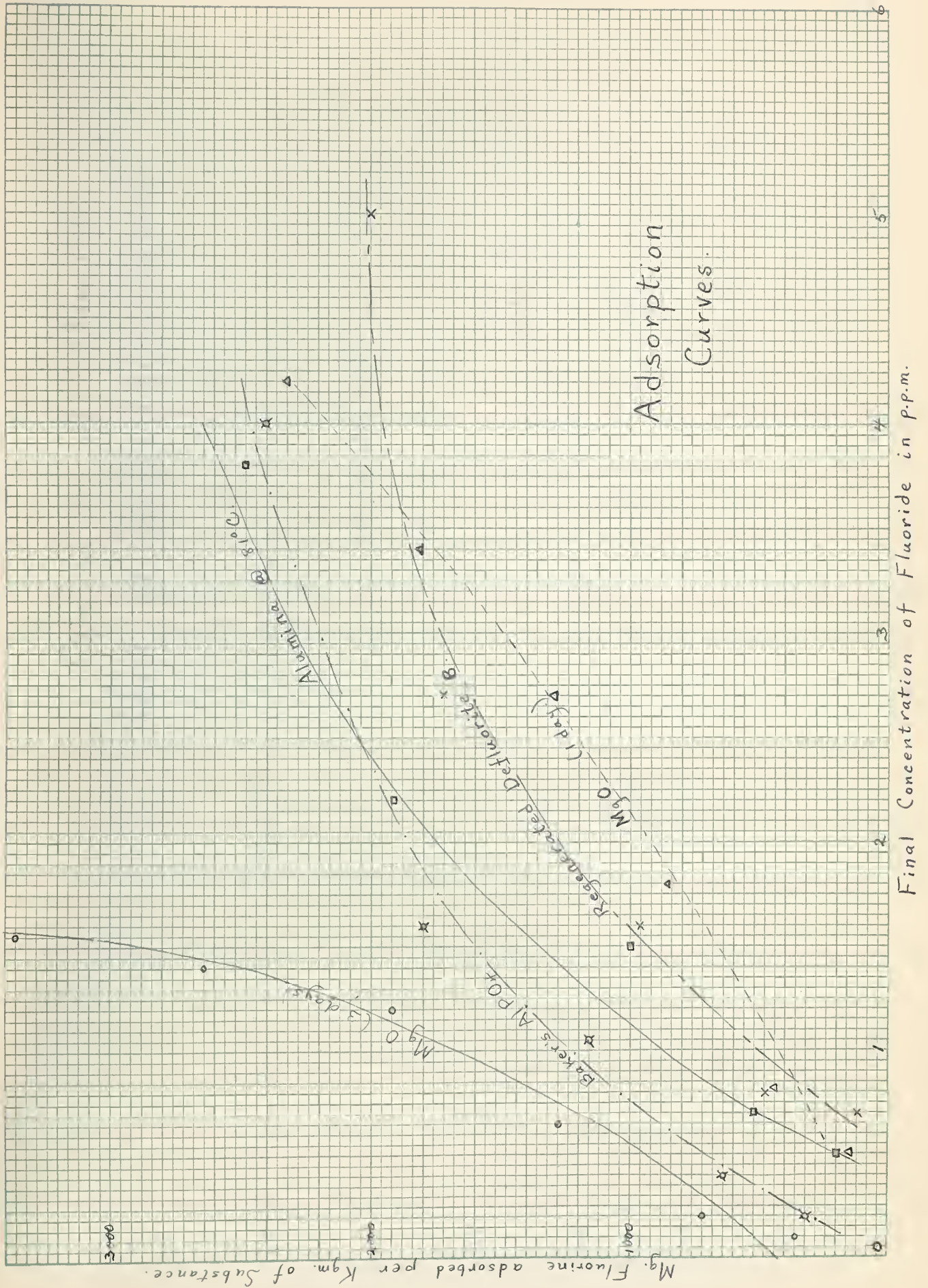




Figure VIII.

# Operation of Defluorite Unit at Harris Farm, Gwynne.

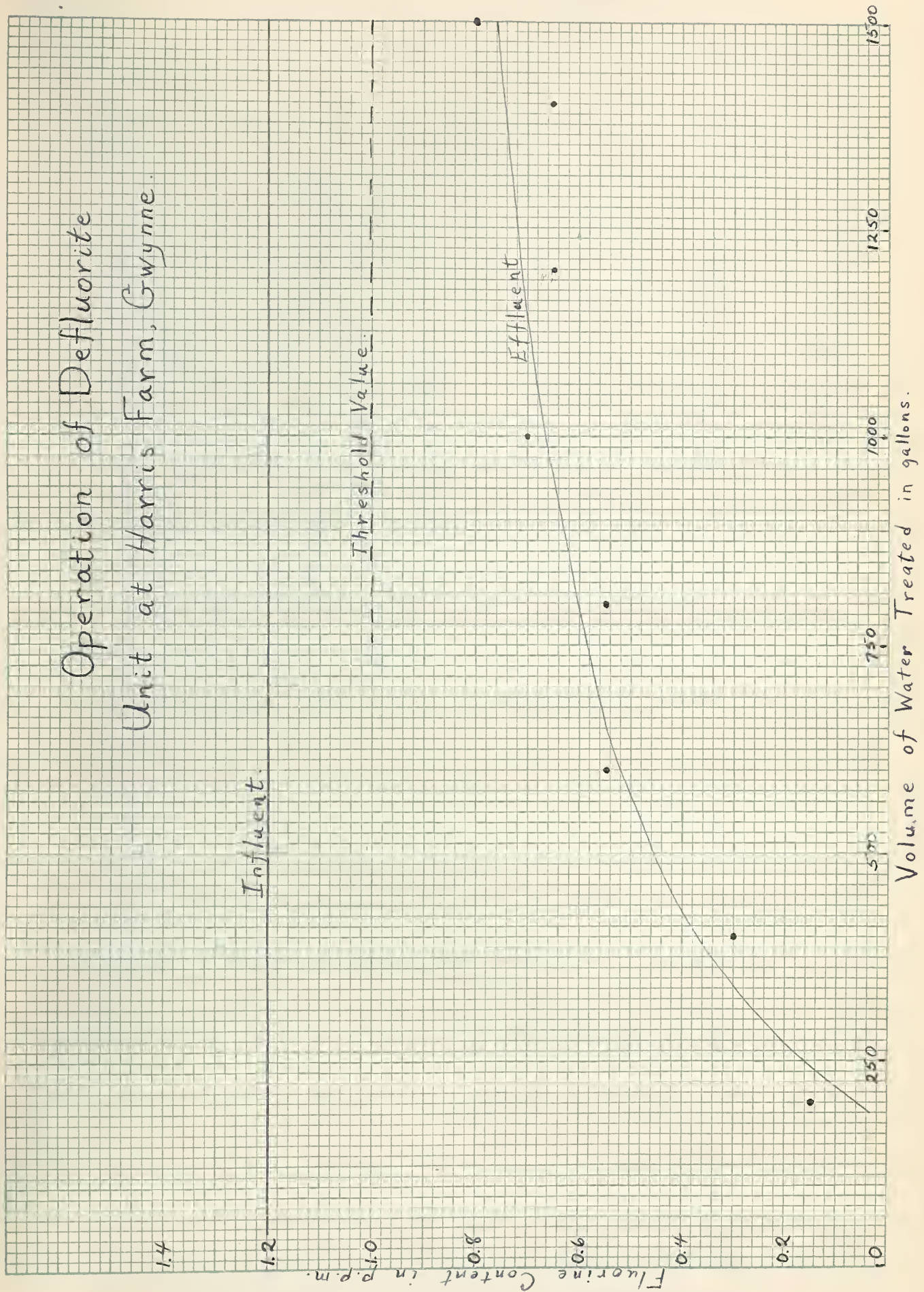
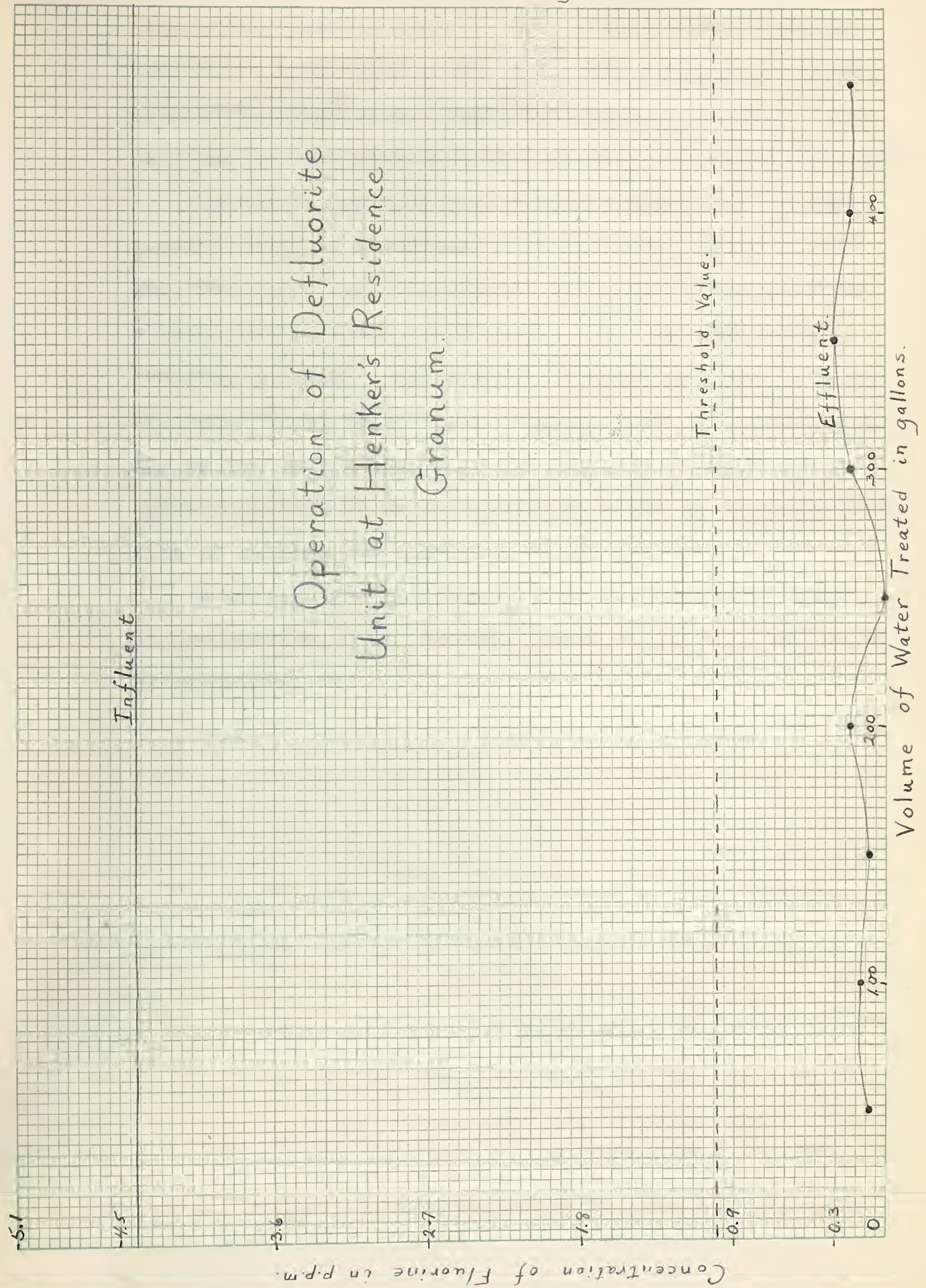




Figure IX.





Regeneration was carried out with dilute sodium hydroxide and dilute hydrochloric acid according to the directions accompanying the unit. Tests were made on small portions in order to make sure that the capacity was fully recovered.

This unit operated quite efficiently and would have probably removed fluorides up to its rated capacity (900 gal. for 4.3 p.p.m. fluoride in influent) if it had been allowed to treat that much water. The treatment also rendered the water soft although it had initially a hardness equivalent to 22 p.p.m.  $\text{CaCO}_3$ . This loss of hardness may be due to the dissolving of phosphates which occurs in quite considerable amounts (see Table VI) or to the adsorption of calcium and magnesium on the defluorite.

A unit is now in operation at the Provincial School of Agriculture, Olds, treating water containing 1.9 p.p.m. of fluorides.



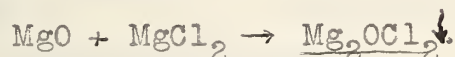
The removal of fluorides may take place either as a simple adsorption on a surface, or by reason of an anion-exchange reaction, or by a direct reaction in which an insoluble substance is formed.

Removal by the defluorite B has been attributed (45) to the tendency to form the complex compound fluorapatite in place of the hydroxyapatite. This might occur either as an anion-exchange or as a molecular exchange.

In the case of magnesium oxide there exists the possibility of the reaction,



analogous to the well-known reaction



The fact that magnesium oxy-chloride has no power to remove fluorides is some evidence in support of this suggestion.

For the other materials which remove fluorides the only mechanism which suggests itself is adsorption on a surface. Actually, the Freundlich adsorption isotherm may be applied with moderate success to the defluorite B, alumina and aluminum phosphate. Freundlich's equation is of the form:

$$\frac{x}{m} = kc^n$$

where  $x$  = weight of substance adsorbed.

$m$  = weight of adsorbent used.

$c$  = final concentration.

and  $k$  and  $n$  are constants characteristic of the substances used.



The constants of the materials listed above and magnesium oxide have been determined over the range of fluorine concentration 1 - 10 p.p.m. The ratio  $\frac{x}{m}$  is then the number of milligrams of fluorine adsorbed by a kilogram of material. The equations obtained are listed below. The adsorption curves from which the equations were obtained are given in Figure VII. The magnesium oxide curves are of a form different from the others, and the equation obtained is a poor fit.

Magnesium Oxide

$$\frac{x}{m} = 500 \text{ c. (one day in contact.)}$$

$$\frac{x}{m} = 2100 \text{ c}^{1.35} \text{ (3 days in contact.)}$$

Bakers Aluminum Phosphate

$$\frac{x}{m} = 1000 \text{ c}^{0.6}$$

Alumina dried @ 81 C.

$$\frac{x}{m} = 320 \text{ c}^{0.7}$$

Regenerated defluorite B

$$\frac{x}{m} = 700 \text{ c}^{0.9}$$

These results are surprising when compared with those previously obtained. The effect of time of contact on the behavior of magnesium oxide is marked and requires further study. It had previously been believed that equilibrium might be attained in one day, but certainly this is not the case when magnesium oxide is employed. The alumina apparently requires an induction period of contact with water before it can become fully effective.



The value of  $\frac{x}{m}$  above is far too low to explain the graphs for alumina in Figures IV and V. Further determinations are to be made on air-dried alumina and air-dried aluminum phosphate.

It is felt that the only materials, other than those classified above as efficient fluoride-removers, which are deserving of future investigation are the anion-exchange resins, the complex aluminum borates and, possibly, zirconium hydroxide. It is quite possible that a resin with an anion-exchange specificity for fluorides may be found which might be used for potable waters. Search for such an one should be made.



### Summary

The most recent reports of the large amount of work being done on the problem of chronic dental fluorosis have been reviewed, and the salient features have been presented.

The limitations of the various methods for determination of fluorine in water have been carefully studied and described. Three procedures developed by Gad and Naumann have been translated and recorded. A table of corrections for the modified Sanchis method in cases in which sulfates are present in quantity has been prepared. Further modifications of the Armstrong method have been made. A method has been proposed for the determination of small amounts (100-200 p.p.m.) of fluorine in soils and several samples have been analysed.

The information collected during the year as to fluoride content of waters and prevalence of "mottled teeth" has been presented. Maps have been prepared to indicate the state of the survey in endemic areas. The results of fluorine analyses have been classified according to source. Certain correlations have been observed between fluorine content of water and depth of well, geological formation, and pH. The possible origin of fluorine in water has been discussed.

A number of materials have been tested for ability to remove fluorides from water. Two new materials for this purpose (aluminum phosphate and a mixture of calcium carbonate and alumina) have been prepared and found to be



satisfactory. The procedure for using a number of other materials has been simplified, and comparative tests have been made using this procedure. The temperature of drying (i.e. the water content) of materials has been shown to exert a marked influence on the power of removing fluorides. Two field tests have been carried out on the operation of "defluorite" units. One test was quite satisfactory, the other only moderately so. The mechanism of removal of fluorides has been discussed and equations representing approximately the behavior of several substances have been presented.

It seems clear that detailed surveys should be undertaken in the several endemic areas so that full information may be available to the people who are concerned with this problem. In most areas water supplies low in fluorine are available and information on fluoride content would there be all that was necessary to prevent "mottled teeth." In other cases the only available supplies may be above the threshold value, and then treatment should be applied. Since only the children's drinking water need be treated, the remedy is simple. The whole problem is to collect the data as to fluorine content and to inform the people concerned as to what may be done to prevent dental fluorosis.



Addendum

A report is now available on the operation of the defluorite unit which, as previously mentioned (p. 35), was placed at the Provincial School of Agriculture, Olds. The water is of the following composition:

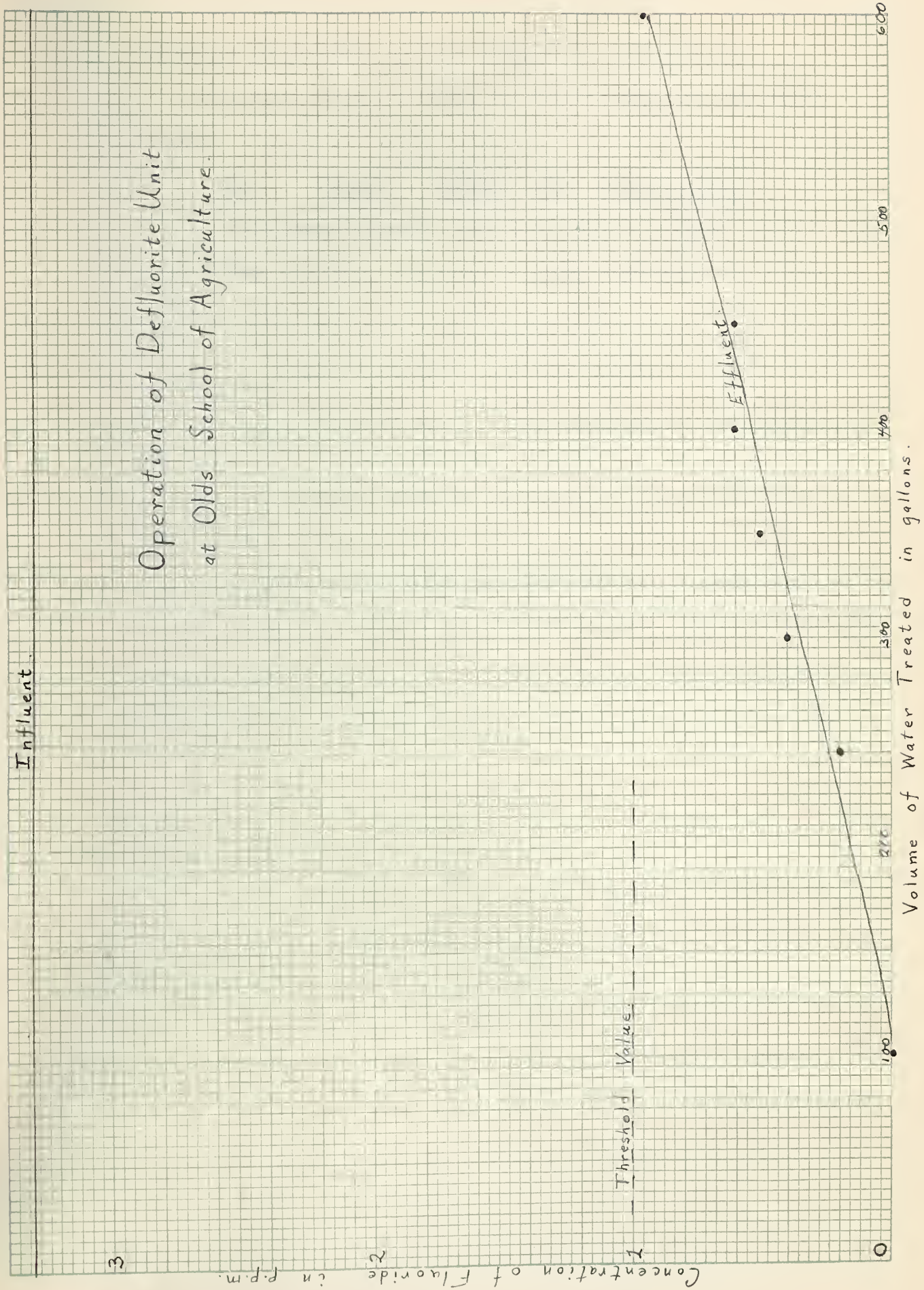
|                                                      |            |
|------------------------------------------------------|------------|
| Total Solids @ 105°C.                                | 880 p.p.m. |
| Loss on ignition                                     | 180        |
| Hardness as CaCO <sub>3</sub><br>(by soap titration) | 18         |
| SO <sub>4</sub> <sup>=</sup>                         | 15         |
| Cl <sup>-</sup>                                      | 8.6        |
| Bicarbonate Alkalinity                               | 662        |
| Carbonate Alkalinity                                 | 3          |
| F <sup>-</sup>                                       | 3.3        |
| pH                                                   | 8.3        |

The effect of the operation of this unit on the fluoride content is shown in Figure X. As in previous operations the effluent was softened. (Sample taken after 200 gal. had been passed through contained 8 p.p.m. hardness; after 350 gal. sample contained 2 p.p.m. hardness). Phosphates were found in the effluent as before. The operation is considered to be fairly satisfactory in this case. Six hundred gallons were treated, compared to a rated capacity for treating twelve hundred gallons. The effluent was clear and as pleasant to the taste as might be expected of a soda water.

From Halcourt has come a report of a family in which the children have mottled enamel. The water supply



Figure X.





contains fluorides to the extent of 4.4 p.p.m.

Two more samples high in fluorides are reported below.

| <u>No.</u> | <u>Place</u> | <u>Depth</u> | <u>pH</u> | <u>F in p.p.m.</u> |
|------------|--------------|--------------|-----------|--------------------|
| 793        | Nobleford    | 150          | 8.2       | 2.1 (corr.)        |
| 798        | Olds         | --           | 8.1       | 3.2 (corr.)        |



## ACKNOWLEDGEMENT

This investigation has been carried out in the Department of Chemistry of the University of Alberta under a Robert Tegler Foundation Research Scholarship.

For much helpful advice and criticism the author is deeply indebted to Dr. Walker.

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Acknowledgement is due Mr. W. E. Harris and Mr. G. A. Henker for their help in operating the fluoride-removal units. Many others have assisted by collecting samples or by furnishing evidence of mottled enamel.



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